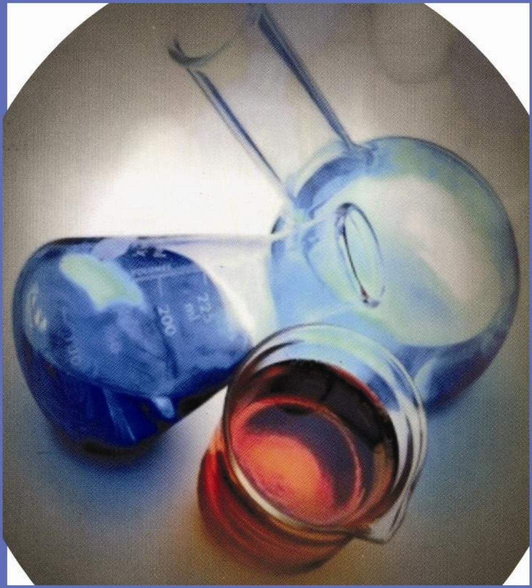
PHYSICAL CHEMISTRY

VOL-III



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PHYSICAL CHEMISTRY

Vol. III

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UNIT-1

SPECTROSCOPY AND ROTATIONAL SPECTRUM

Introduction, electromagnetic radiations, regions of the spectrum, basic features of different spectrometers, statement of Born-Oppenheimer approximation, degrees of freedom.

Rotational spectrum : Diatomic molecules, energy levels of a rigid rotor (semi-classical principles), selection rules, spectral intensity, distribution using population, distribution (Maxwell-Boltzmann distribution), determination of bond length, qualitative description of non-rigid rotor, isotope effect.

PROBLEMS

Problem1. ***Give an introduction of spectroscopy. Mention the electromagnetic radiations.***
Or, Relate the units : Micron, Angstrom and Nanometre.
(Meerut 2007, 2006)

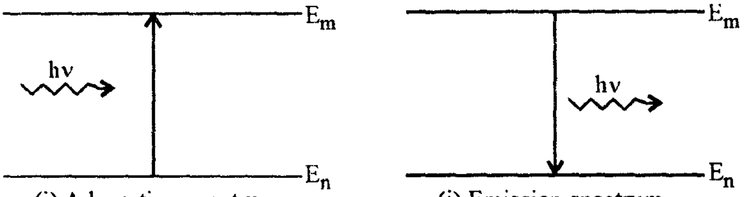
[I] SPECTROSCOPY

In organic chemistry, the most commonest and most important job is to determine the structural formula of a compound just synthesised or isolated from a natural source. The compound will fall into one of the two groups though at first we shall not know which group? It will be either (i) a previously reported compound, which we must identify or (ii) a new compound, whose structure we must prove.

If the compound has already been reported by some other chemists, then a description of its properties will be found somewhere in the chemical literature. We then have to show that the compound prepared is identical with the one previously described. If, on the contrary, our compound is a new one that has never before been reported then we must carry out a much more elaborate proof of its structure. To carry out our investigations, we first purify the compound and determine its physical properties like melting point, boiling point, density, refractive index and solubility in different solvents. In the laboratory today, we would measure various spectra of the compound, in particular, the infrared spectrum and the NMR spectrum because spectroscopic examination gives us a wealth of informations.

Spectroscopy is a technique ***which deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by quantum mechanical selection rules.***

Quantum mechanics tells us that the energy levels of all systems are quantized which are given by suitable quantum numbers. These energy levels are obtained by solutions of the time-independent Schrödinger wave equation. We now consider how a spectrum arises ? In figure (1), the two molecular energy levels are shown as E_n and E_m. If a photon of frequency ν falls on



(i) Adsorption spectrum (i) Emission spectrum

Fig. 1. Spectroscopic transitions between molecular energy levels.

a molecule in the ground state and its energy $h\nu$ is exactly equal to the energy difference ΔE ($= E_m - E_n$) between the two molecular energy levels, then the molecule undergoes a transition from the lower energy level to a higher energy level due to absorption of a photon of energy, $h\nu$. he spectrum thus obtained is known as **absorption spectrum**. If on the contrary, the molecule undergoes a transition from the excited energy level to the ground state with the emission of a photon of energy, $h\nu$, the spectrum thus obtained is known as **emission spectrum**.

The instruments most directly concerned with our primary interest, molecular structure, are the *spectrometers*–measures of spectra. The spectroscopic methods have several advantages over the classical methods of analysis which are as follows :

(a) Spectroscopic methods take much less time.

(b) For spectroscopic analysis, only a very small amount of the substance, say 1 mg or even less, is sufficient.

(c) The substances remain generally unaffected or unchanged during spectroscopic examination and can be re-used for other tests, if required.

(d) The spectroscopic methods are comparatively much reliable in establishing the structure and identity of a compound.

Table 1 : Symbols used in spectroscopy

Symbol	Definition
ν	Frequency in Hz (cycles per second)
λ	Wavelength
μ	Micrometre, as micron (μ), 10^{-6} m
nm	Nanometre, as millimicron (mμ), 10^{-9} m
Å	Angstrom, 10^{-10} m or 10^{-1} nm
cm^{-1}	Wave number, Frequency in reciprocal cm or $\frac{1}{\lambda} = \text{cm}^{-1}$

[II] ELECTROMAGNETIC RADIATIONS

We are already familiar with different kinds of electromagnetic radiation of light (visible, ultraviolet, infrared), X-rays, radio and radar waves. These are simply different parts of a broad spectrum that stretches from gamma rays, whose wavelengths are measured in fractions of an angstrom, to radiowaves, whose wavelengths are measured in metres or even kilometres. All these have the same velocity, 3×10^{10} centimetre per second.

Mathematically, wavelength (λ) of a radiation is related to its frequency (ν) by the expression.

$$\lambda = \frac{c}{\nu}$$

where c is the velocity of the radiation and is equal to 3×10^{10} cm/sec. As λ and ν are inversely related to each other, the shorter the wavelength, the higher the frequency and vice-versa.

Table 2 : Wavelength of electromagnetic radiations

Radiation	Wavelength (Å)		
Cosmic rays	Zero	to	0.001
Gamma rays	0.001	to	0.1
X-Rays	0.1	to	150
Ultraviolet rays	150	to	3800
Visible rays	3800	to	7600
Infrared rays	7600	to	6×10^6
Microwaves	6×10^6	to	3×10^9
Radiowaves	3×10^9	to	3×10^{13}

When a beam of electromagnetic radiation is passed through a substance, the radiation can be either absorbed or transmitted, depending upon its frequency and the structure of the molecules it encounters. Electromagnetic radiation is energy, and so when a molecule absorbs radiation, it gains energy. Just how much energy it gains, depends upon the frequency of the radiation. The higher the frequency (the shorter the wavelength) the greater the gain in energy. The gain in energy (ΔE) and frequency of radiation are connected by the following relation

$$\Delta E = h\nu$$

where h is Planck's constant (6.626×10^{-27} erg sec). As ΔE and ν are directly related, radiation with higher frequency (or shorter wavelength) leads to a greater gain in energy. In other words, the shorter the *wavelength of a radiation, the more energetic it is.*

The units commonly used to express the wavelengths of ultraviolet, visible and infrared radiations are Greek symbols, **micron** (μ) and **millimicron** ($m\mu$).

$$1\mu = 1000\ \text{m}\mu = 10^{-4}\ \text{cm.}$$

Occasionally, the unit **Angstrom** (Å) is used to denote especially ultraviolet and visible radiations.

$$1\ \text{Å} = 0.1\ \text{m}\mu = 10^{-4}\ \mu = 10^{-8}\ \text{cm.}$$

More recently, the wavelength of ultraviolet and visible radiations are expressed in **nanometres (nm).**

$$1\ \text{nm} = 1\ \text{m}\mu = 10^{-3}\mu = 10\ \text{Å.}$$

The frequency is usually expressed in **Hertz** (Hz), or cycle/second.

$$1\ \text{Hz} = 1\ \text{cycle/second.}$$

Sometimes, molecular spectra are expressed in frequency units which are **reciprocal centimetres** (cm^{-1}). A reciprocal centimetre shows the number of wavelengths per centimetre and is known as **wave number** ($\bar{v}$).

Wavelength in μ units can be converted into wave numbers (cm^{-1}) by the following expression:

$$\text{Wave number } (\text{cm}^{-1}) = \frac{10^4}{\lambda\ (\text{in}\ \mu)}$$

The approximate range of wavelengths, frequencies and energies of different types of radiations are given in table 3.

Table 3

Types of radiation	Wavelength (Å) (Upper limit)	Frequency (Hz or s^{-1})	Energy (kJ mol^{-1})
Cosmic rays	0.001	3×10^{21}	1.2×10^9
Gamma rays	1	3×10^{16}	1.2×10^6
X-rays	150	2×10^{16}	8.98×10^3
Ultraviolet	38.0	7.9×10^{14}	3.16×10^2
Visible	7600	3.95×10^{14}	1.58×10^2
Infrared	6×10^6	5×10^{11}	1.99×10^{-1}
Microwaves	3×10^9	10^9	3.99×10^{-4}
Radiowaves	3×10^{13}	10^5	3.99×10^{-8}

Problem 2. ***What are the different regions of spectrum?***

[I] Origin and Regions of Electronic Spectra

Electronic spectra can be classified into following two types :

(a) Emission spectra

(b) Absorption spectra

(a) Emission Spectra : When a substance is subjected to a large amount of heat or to an electric discharge, its atoms or molecules absorb energy and are excited. When these excited species return to their ground state, they may emit radiation which on passing through a prism gives rise to a spectrum, known as **emission spectrum**. If such a spectrum is recorded on a photographic plate, the atoms in it appear as bright lines on a dark background, and that of molecule appear as bands.

(b) Absorption Spectra : If we place a coloured substance between the prism and the source of light, a portion of the light in the continuous spectrum may be absorbed and we get black bands. If, for example, a sodium flame is placed between white light source and the prism, the continuous spectrum of white light is crossed by two dark lines in the yellow region. If white light source is now removed, the whole of continuous spectrum disappears leaving behind only two bright yellow lines occupying the position of the two dark lines in the former case. These dark lines are called ***absorption line spectrum*** or simply ***absorption spectrum.***

During absorption, some of the molecules in the path of incident light collide with photons of radiant energy. However, only those photons get absorbed whose energy exactly equals the difference in energy, ΔE between the ground and excited states of the molecules.

[II] Types of Absorption Spectra

The internal energy of a molecule may be considered to be the sum of electronic, vibratioal, rotational and translational energies, *i.e.*,

$$E_{\text{internal}} = E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}$$

Translational energy is not quantized so it is negligibly small and we can neglect it, hence

$$E_{\text{internal}} = E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}}$$

(1) Ultraviolet (UV) spectroscopy : For each electronic level within the molecule there is an energy separation of nearly 10^5 cal mole^{-1}. Therefore, electronic excitation requires energetic photons of $\lambda \sim 286$ nm from ultraviolet range (200-400 nm). This is called *ultraviolet (UV) spectroscopy.*

(2) Infrared (IR) spectroscopy : We find a number of associated vibrational levels between two successive electronic levels X and Y, the energy separation between the former levels is one tenth to a hundredth of that between X and Y. Further, each vibrational level is associated with a set of rotational states and the energy separation is of the order of a hundredth of that between two vibrational levels.

Photons from IR range (2000 to 20,000 nm) possess sufficient energy to excite the molecule from one vibrational level to another. In IR spectroscopy, the radiation absorbed produce *stretching* and *bending* of organic bonds.

(3) Nuclear magnetic reasonance (NMR) spectra : The wavelength of radiations absorbed by atomic nuclei are under the influence of strong magnetic fields. Thus, NMR spectra span the radio-frequency regions, *viz.*, 5–100 MHz which induce transitions between the nuclear spin energy levels of a molecule.

Problem 3. ***Describe the basic features of different spectrometers.***

The schematic diagram of the apparatus for absorption spectroscopy is given in Fig. (2).

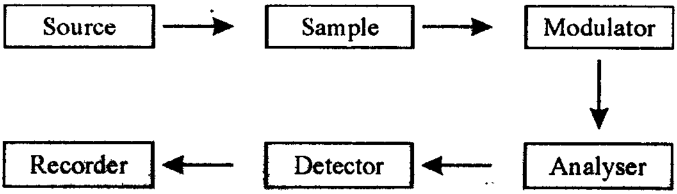


Fig. 2. Apparatus for absorption spectroscopy.

The spectrometer is employed when absorption occurs in infrared and ultraviolet regions of the electromagnetic spectrum. The source in a spectrometer produces radiation spanning a range of frequencies, but in a few cases, it is almost a monochromatic radiation. The radiation source in an absorption spectrometer consists of a heated ceramic filament coated with the rare earth oxides for the infrared region. For visible region of the spectrum, the source is a tungsten filament which gives out intense white light. For ultraviolet region, the source is a hydrogen discharge lamp. To generate microwaves, *klystron* or more commonly, a semiconductor device called *Gunn diode* is used. The radio frequency radiation is produced by causing an electric current to oscillate in a coil of wire.

The variation of absorption with frequency is determined by analysing the spectral radiation by means of a dispensing element which separates different frequencies into rays that travel in different directions. The simplest dispensing element consists of a glass or quartz prism, but a diffraction grating is widely used. Diffraction grating consists of a glass or ceramic plate into which fine grooves have been cut nearly 1000 nm apart (a spacing comparable to the wavelength of visible light) and covered with a reflective aluminium coating. The grating produces interference between waves reflected from its surface and constructive interference occurs at specific angles that depend on the frequency of the radiation used. So, each wavelength of light is directed into a specific direction.

The third component of spectrometers is the *detector.* It is a device that converts the spectral radiation into an electrical signal that is passed on to a recording device operating synchronously with the analyzer. It thus produces either a trace on a chart recorder or a computer record of the spectrum. Common detectors are the radiation sensitive semiconductors. The radiation is chopped by a shutter which rotates in the beam so that an alternating signal is produced from the detector. A modulator is introduced to change the signal to an alternating character. This method helps more AC electronics to be used in in the recording stages. In the microwave region, the source frequency is varied and the analyser is not necessary.

The highest resolution is obtained when the sample is gaseous and at such low pressure that collisions between molecules are not frequent. In order to get sufficient absorption, the path lengths of gaseous samples must be very long, of the order of metres. Long path lengths are obtained by multiple passage of the beam between two parallel mirrors at each end of the sample cavity. For infrared spectroscopy, the sample is a liquid held between windows of sodium chloride (which is transparent down to 700 cm^{-1}) or potassium bromide (down to 400 cm^{-1}). Other methods of preparing the sample include grinding it into a paste with 'Nujol', a hydrocarbon oil, or pressing it into a solid disk with powdered potassium bromide.

Problem 4. ***What are different laws which govern spectroscopy? How is spectral data presented?***

[I] Laws of Light Absorbance

The electronic spectra of organic compounds are usually recorded in solution and involves the use of the following laws :

(1) Lambert's law : When a homogeneous absorbing medium absorbs monochromatic radiation, then the rate of decrease of intensity of radiation with thickness of the absorbing medium is directly proportional to the intensity of the incident radiation, *i.e.*,

$$-\frac{dI}{dx} \propto I$$

or
$$-\frac{dI}{dx} = kI \qquad \text{... (1)}$$

where I = Intensity of radiation after passing through a thickness, x

dI = change in intensity on passing through a small thickness, dx

k = absorption coefficient.

Equation (1) can be written as

$$\frac{dI}{I} = -kdx$$

or
$$\int_{I_0}^{I} \frac{dI}{I} = -k\int_0^x dx$$

or
$$\log_e \frac{I}{I_0} = -kx \qquad \text{... (2)}$$

or
$$\frac{I}{I_0} = e^{-kx}$$

or
$$I = I_0 \, . \, e^{-kx} \qquad \text{... (3)}$$

where I_0 is intensity of incident radiation and I is its intensity after travelling through a medium of thickness x.

Equation (2) can also be written as,

$$2.303 \log_{10} \frac{I}{I_0} = -kx$$

or
$$\log_{10} \frac{I}{I_0} = \frac{-k}{2.303}x = -ax$$

or $$\frac{I}{I_0} = 10^{-ax}$$

or $$I = I_0 \, . \, 10^{-ax}$$

where, $$a = \frac{k}{2.303}$$

where a = extinction coefficient of the absorbing medium.

(2) **Beer's law** : When a solution of an absorbing substance absorb radiations of monochromatic light, then the rate of decrease of intensity of radiation is proportional to the intensity of incident radiation as well as the concentration of the solution

$$-\frac{dI}{dx} \propto Ic$$

$$-\frac{dI}{dx} = k' \, Ic$$

where, c = Concentration of the solution in mole/litre

k' = molar absorption coefficient and its value depends upon the nature of the absorbing substance.

On proceeding as in Lambert's law, we get

$$\log \frac{I}{I_0} = -\,\varepsilon cl$$

or $$\log \frac{I_0}{I} = \varepsilon cl$$

or $$A = \varepsilon cl$$

where $A = \log \frac{I_0}{I}$ = optical density or absorbance of the solution

I_0 = intensity of incident light

I = intensity of transmitted light

c = concentration (mole lit^{-1}) of solution containing the absorbing substance

l = length (cm) of the sample tube containing the solution

ε (epsilon) = absorptivity coefficient or molecular extinction coefficient at a particular wavelength.

If T is the transmittance of the solution, then $T = I/I_0$. The wavelength at which a molecule possesses its highest absorptivity

coefficient (ε_{max}) is denoted by λ_{max}. A spectra of any compound may contain several different maxima each with its characteristic value of ε_{max}, as shown in figure (3).

The infrared spectrum, for example, exhibits several sharp peaks, whereas its ultraviolet spectrum shows only a broad band. In general also, ultraviolet-visible spectra shows only a few broad bands, but IR spectra are usually complex exhibiting a series of sharp peaks.

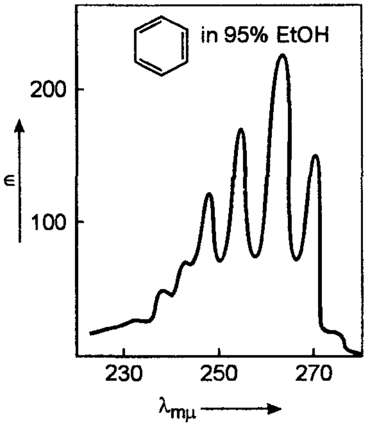


Fig. 3.

[II] Presentation of Spectral Data

A graph plotted between absorbance or absorptivity (ε or log ε) and wavelength (in nm represents the absorption spectrum of an organic compound. We measure only the values of ε_{max} and λ_{max}. If the molecular weight is unknown, ε cannot be calculated. In such a case, log (I_0/I) or $E^{1\%}_{1\,cm}$ for 1% solution or 1 cm path length is plotted against wavelength. Absorption minima and absorption maxima are those points on the absorption curve at which the absorbance attains a minimum or maximum value, respectively. An inflexion is produced when a discontinuity or a shoulder appears on a curve of increasing or decreasing absorbance. As already written, the instrument used for measuring the amount of light absorbed at each wavelength of the incident radiation is known as ***spectrometer***. A ***spectrograph*** is an instrument which makes a photographic record of the spectrum. A ***spectrophotometer*** is an instrument which involves the use of a photoelectric cell to provide a quantitative measure of the light intensity of each wavelength.

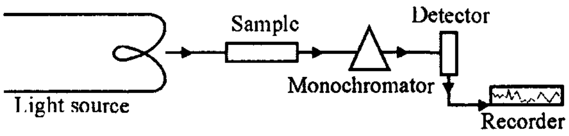


Fig. 4.

Problem 5. ***Discuss the different types of energy transitions.***

Electronic transitions for organic molecules involve absorption of ultraviolet or visible radiation by electrons in σ, n or π-orbitals and results in their promotion to some higher energy antibonding orbital (excited state).

The transitions are $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ when selection rules are applied, $n \rightarrow \pi^*$ transition is forbidden, while only $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions are allowed.

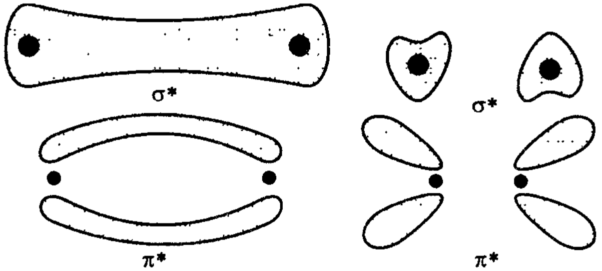


Fig. 5. Bonding and antibonding molecular orbitals.

The energy level scheme for a molecule is shown in figure (6). From the figure, it is evident that energy values for different transitions are in the following order.

$$n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* < \sigma \rightarrow \sigma^*$$

The main features of all the above mentioned transitions are mentioned below :

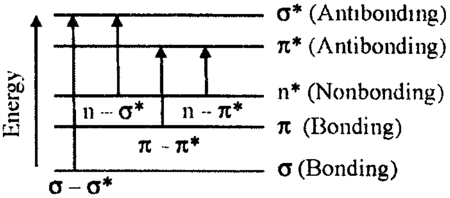


Fig. 6. Energy levels and transitions in simple organic molecules.

(1) $\sigma - \sigma^*$ Transitions : These transitions occur in only those compounds in which all the electrons are involved in single bonds and no lone pairs of electrons are available, *e.g.*, saturated hydrocarbons. The energy required for $\sigma \rightarrow \sigma^*$transitions is appreciably large, so the absorption band occurs in the far ultraviolet region (125-135 nm), *e.g.*, methane and ethane show a bond at $\lambda_{\max} \sim 121.9$ nm and 135 nm, repectively, corresponding to $\sigma - \sigma^*$ transition.

Such transitions cannot normally be observed by commercial spectrophotometers, as they do not generally operate at wavelengths less than 180-200 nm.

(2) $n \to \pi^*$ Transitions : These transitions are shown by unsaturated molecules which contain atoms such as nitrogen, oxygen, sulphur etc. These transitions show a weak band in their absorption spectrum. As there are no $C=C$ and $C\equiv C$ bonds in aldehydes and ketones, the band due to $n \to \pi^*$ transition generally occurs in the range 270-300 nm (2700-3000 Å). On the contrary, carbonyl compounds having double bonds separated by two or more single bonds show $n \to \pi^*$ transition in the 300-350 nm range.

The general characteristics of $n \to \pi^*$ bonds are low intensity (normally less than 1500) and are shifted to shorter wavelengths by more polar solvents as well as by electron donating groups. In the spectra of simple molecules, $n \to \pi^*$ transitions require the least energy and the corresponding bands are of longest wavelength.

In aldehydes and ketones, the $n \to \pi^*$ transition arises due to the excitation of a lone pair of electrons in the $2p_y$ orbital of the oxygen atom into the antibonding π^* orbital of the carbonyl group. On replacing the hydrogen atom by a methyl group in aldehyde group, a shift of band is observed due to $n \to \pi^*$ transition to shorter wavelengths.

$$\mathrm{C{=}\ddot{O}\!:} \;\longrightarrow\; \mathrm{>\dot{C}=\dot{O}\!:}\ (n \to \pi^*)$$

(3) $\pi - \pi^*$ Transitions : These transitions involve the excitation of an electron from a bonding π-orbital to an antibonding π^* orbital. Molecules which have a π electron system show $n \to \pi^*$ transitions. However, selection rules determine whether a transition to a particular π^* orbital is allowed or forbidden. Simple chromophores consisting of multiple bonded units such as $-\overset{|}{C}=\overset{|}{C}-$, $-C\equiv C-$, $-C\equiv N$, $-N=N-$, $-\overset{|}{C}=O$, undergo $\pi \to \pi^*$ transitions in short wavelength regions of ultraviolet light. When a π electron is excited by ultraviolet radiation, it moves from a stable (bonding) π orbital to an unstable π (π^*) orbital, as shown below :

$$\mathrm{C{=}\ddot{O}\!:} \;\longrightarrow\; \mathrm{>\dot{C}{-\!\!-\!\!-}\ddot{O}\!:}\ (\pi \to \pi^*).$$

In the spectrum of ethylene, an intense band occurs at ~ 174 nm and a weak band at ~ 200 nm. Both these bands are due to $\pi — \pi^*$ transitions. According to selection rules, the band at ~ 174 nm shows an allowed transition. The intensity of absorption by ethylene is mainly independent of the solvent because of non-polar nature of the olefinic bond. Alkyl substitution of the olefins makes the absorption to occur at a longer wavelength. This effect is known as *bathochromic effect* (a red shift). This effect is progressive as the number of alkyl groups increases. The ultraviolet absorption spectrum of benzene shows three bands, a weak band at ~ 260 nm and two intense bands at ~ 180 – 200 nm.

(4) $n \rightarrow \sigma^*$ Transitions : In addition to $\sigma \rightarrow \sigma^*$ transitions, saturated organic compounds with lone pair (non-bonding) electrons undergo $n \rightarrow \sigma^*$ transitions. The energy required for $n \rightarrow \sigma^*$ transition is generally less than that required for a $\sigma \rightarrow \sigma^*$ transition and the absorption bands appear at longer wavelengths in the near ultraviolet (180-200 nm) range. Some compounds absorb at slightly longer wavelengths. Methyl chloride, methyl alcohol and trimethylamine show the characteristics of $n \rightarrow \sigma^*$ transitions.

Problem 6. ***Explain the following terms :***

(i) Chromophores **(Meerut 2005)**
(ii) Auxochromes **(Meerut 2005)**
(iii) Spectroscopic shifts.

[I] Chromophores

Chromophores are any isolated covalently bonded groups that absorb selective wavelengths and even small structural changes bring about perceptible changes in the radiation absorbed, *e.g.*, ethylenic, acetylenic, carbonyls, acids, esters, nitrile groups etc.

[II] Auxochromes

Auxochrome is any group which does not itself act as a chromophore, but whose presence brings about a shift of the absorption band towards the red end of the spectrum, *e.g.*, —OH, —OR, $—NH_2$, —NHR, $—NR_2$, —SH etc.

The chromophore is any system which is responsible for imparting colour to the compound, while auxochrome is colour enhancing group. It extends the conjugation of a chromophore by the sharing of non-bonding electrons.

[III] Spectroscopic Shifts

The protonation of a functional group introduces profound changes in the spectra. Thus, the spectrum in such cases is strongly dependent upon pH. Solvent effects, too, are useful in identifying the nature of these transitions. The $n \rightarrow \pi^*$ transitions are altered by the solvent effects in cases where the lone pair of electrons in oxygen or nitrogen-containing systems interact with polar solvents. It is customary in spectroscopic literature to refer to the shifts in absorption bands and their intensity changes are as follows :

(1) Bathochromic shift (or, the red shift) : A shift of λ_{max} to longer wavelengths.

(2) Hypsochromic shift (or, the blue shift) : A shift of λ_{max} to shorter wavelengths.

(3) Hyperchromic shift : An increase in the intensity of an absorption band, usually with reference to its molar extinction coefficient ε_{max}.

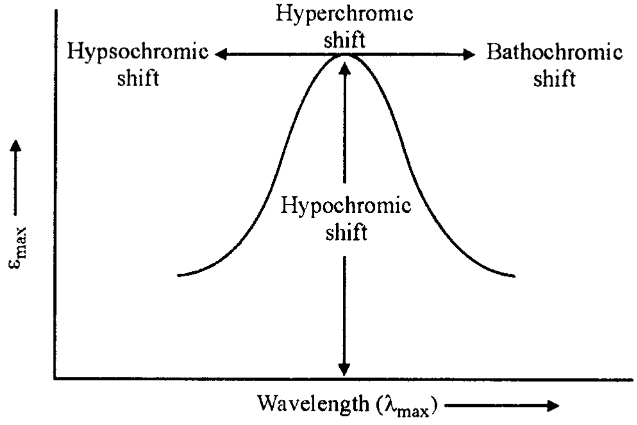


Fig. 7. Shifts of intensity by different absorption.

(4) Hypochromic shift : A decrease in the intensity of an absorption band usually with reference to its molar extinction coefficient ε_{max}.

Problem 7. ***What is UV-spectroscopy? Discuss the origin and theory of ultraviolet spectra.***

Ultraviolet spectroscopy is a technique which is at present commonly used in the detection of impurities in organic compounds. It is also employed in determining the molecular weights, dissociation constants of acids and bases, in the study of kinetics of certain reactions in the ultraviolet range.

The ultraviolet range can be divided into two spectral regions :

(i) The region between 2000 to 4000Å which is known as *near ultraviolet region.*

(ii) The region below 2000Å which is known as *far* or *vacuum ultraviolet region.*

As already mentioned, the wavelengths in the UV region is expressed in nanometre ($1 \text{ nm} = 10^{-7}$ cm) or angstrom ($1 \text{ Å} = 10^{-8}$ cm). The absorption is generally expressed in wave numbers ($\bar{\nu} = \text{cm}^{-1}$).

This spectroscopic technique is not useful below 200 mμ because in this region absorption occurs by oxygen and nitrogen. To study absorption below this region, the whole path length is evacuated. Hence, this region is called vacuum ultraviolet region.

Origin and Theory of Ultraviolet Spectra

The ultraviolet absorption spectrum occurs due to transition of electron within a molecule or an ion from a lower to a higher electronic energy level. The ultraviolet emission spectra occurs due to the reverse type of transition. If the radiation is to cause electronic excitation, it must be in the ultraviolet region of the electromagnetic spectrum.

If a molecule after absorbing ultraviolet radiation of frequency ν sec^{-1}, undergoes transition from a lower to a higher energy level, the energy difference is given by

$$\Delta E = h\nu \text{ erg}$$

where h is Planck's constant.

The actual amount of energy required depends on the difference in the energy between the ground state E_1 and excited state E_2 of the electrons. The above equation now becomes

$$E_2 - E_1 = h\nu$$

The spectra of simple molecules in the gaseous state have narrow absorption peaks, where each peak represents a transition from a particular combination of vibrational and rotational levels in the electronic ground state to a corresponding combination in the excited state. In ultraviolet range, the absorbed energy produces changes in the valency electrons of the molecules.

The electrons involved in organic molecules are as mentioned below :

(i) π-Electrons : These electrons are involved in unsaturated hydrocarbons. Some typical compounds containing π-bonds are trienes and aromatic compounds.

(ii) σ-Electrons : These electrons are involved in saturated bonds between carbons and hydrogens as in paraffins. These bonds are also known as σ-bonds. The amount of energy required to excite electrons in σ-bonds is much more than that produced by ultraviolet light. Compounds containing such bonds, therefore, do not absorb ultraviolet radiation. For this reason, paraffn compounds are usually used as solvents.

(iii) *n*-Electrons : These electrons are not involved in bonding between atoms in the molecules, *e.g.*, organic compounds containing nitrogen, oxygen, sulphur or halogens. As *n*-electrons can be excited by ultraviolet radiation, any compound containing nitrogen, oxygen, sulphur or halogens or unsaturated hydrocarbons may absorb ultraviolet radiations.

Problem 8. ***Discuss the basic features or main components of ultraviolet spectrophotometer.*** **(Meerut 2007, 05)**

The main components of an ultraviolet spectrophotometer are mentioned below :

(1) Radiation source : Generally, a hydrogen-discharge lamp is the source for ultraviolt radiations (200-400 nm), while a tungsten filament lamp is commonly used to produce visible radiations (400-800 nm).

(2) Monochromator : It is used to disperse radiation according to a desired wavelength.

(3) Sample cells : These cells are used to contain samples for analysis. A cell is made up of that material which does not absorb light in the region being studied. Generally, quartz cells are used in the ultraviolet and visible regions.

(4) Detectors : Generally, barrier layer cell, photocell, photo multiplier tube are used.

(5) Recording system : The unknown compound is first dissolved in a suitable solvent at a proper concentration. The solution is then placed in a suitable cell. An identical cell containing only the solvent is used at the same time to serve as the control cell. The cell containing the sample is then exposed to UV or visible radiation of appropriate wavelength. The instruments are so designed that they directly measure the optical density of the solution at the desired wavelength. The wavelength of radiation is then changed, and a new value of optical density is measured. In this way, a number of values of optical density are recorded over a range of wavelengths. A graph is plotted between wavelengths as abscissa and optical density readings (or molar extinction coefficients, ε, as optical density = $\varepsilon, c \,.\, l$) as ordinate. The resulting graph is known as *ultraviolet spectrum*, which may consist of one or more broad peaks or humps. The wavelength corresponding to the top of the peak is taken to be the value of λ_{max}. The values of λ_{max} and ε at the wavelength are shown, while giving UV spectral data of a compound.

In a self recording spectrophotometer, the plotting of graph is done automatically by the movement of a pen on a chart.

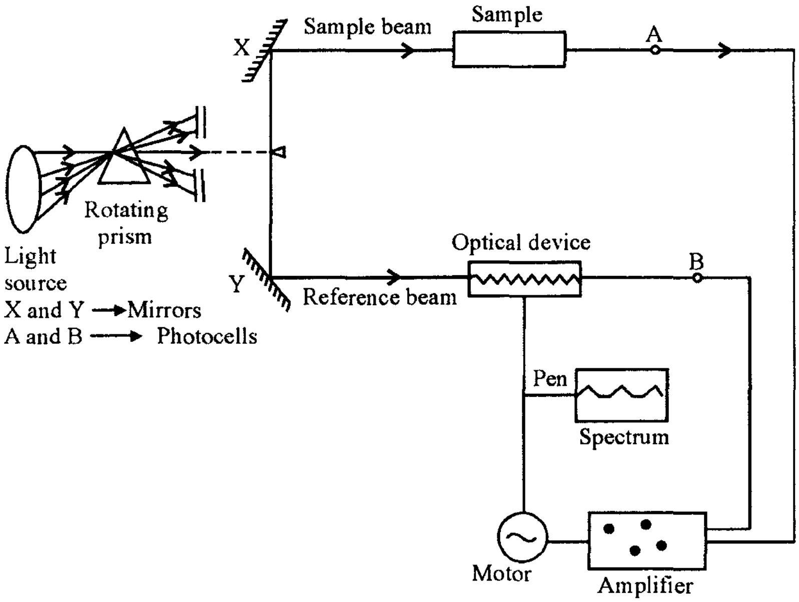


Fig. 8. UV. spectrophotometer

Problem 9. ***Mention some important applications of ultraviolet spectroscopy.*** **(Meerut 2007)**

Some important applications of ultraviolet spectroscopy are as follows :

(1) Qualitative analysis : Identification of compounds can be done by comparing absorption spectrum with known compound. A curve is plotted between wavelengths (λ) and degree of absorption (ε).

(2) **Quantitative analysis** : The technique is also used for quantitative analysis of compounds. This is based on Beer's law. In the determination of concentration of an unknown compound, wavelength of maximum absorption for compound is selected. Then optical densities are measured for some known compounds. Now the optical density is plotted against concentration of solute over a range of concentrations. A straight line is obtained and from this graph, the concentration of unknown solution is evaluated.

(3) **Chemical kinetics** : The technique is helpful for studying the kinetics of a reaction. Here change in concentration of either a reactant or product with time is measured. As absorbance is proportional to concentration, so this technique can be used to follow the course of a reaction.

(4) **Molecular weight determination** : Molecular weights of compounds can easily be determined by this technique provided suitable derivatives of these compounds could be prepared.

Take a picrate and change it into aminopicrate. A known concentration of it is dissolved in one litre of solution and its optical density measured at $\lambda_{max} = 380$ nm. The concentration c is determined by the formula

$$c = \frac{\log \frac{I_0}{I_t}}{\varepsilon_{max} \times l}.$$

From this, c is calculated. The weight w of aminopicrate is known. From c and w, molecular weight of aminopicrate can be calculated. From it, the molecular weight of parent compound can be determined.

(5) **Dissociation constant of acids and bases** : Consider the reaction :

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$

where A^- is conjugate base.

The dissociation constant K can be written as :

$$K = \frac{a_{H_3O^+} \times a_{A^-}}{a_{HA}}$$

where a represents activity.

If solutions are dilute, the activity terms can be replaced by concentrations of the species at equilibrium. So,

$$K = \frac{[H_3O^+]\,[A^-]}{[HA]}.$$

On taking logarithm of both sides,

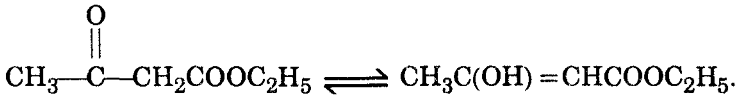
$$\log K = \log [H_3O^+] + \log [A^-]$$

or $$-\log K = -\log [H_3O^+] - \log [A^-] / [HA]$$

or $$pK = \text{pH} - \log \frac{[A^-]}{[HA]} = \text{pH} + \log \frac{[HA]}{[A^-]}.$$

From the above equation, pK can be calculated if $\log [HA] / [A^-]$ is known at a particular pH. The ratio $[HA / [A^-]$ can easily be determined from the graph plotted between absorbance and wavelength at different pH values.

(6) Tautomeric equilibrium : The technique has been proved very helpful in determining the percentages of keto and enol forms in tautomeric equilibrium. Take an example of ethyl acetoacetate.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3C(OH)=CHCOOC_2H_5.$$

The keto form has $\lambda_{max} = 275$ nm and $\varepsilon = 16$, while enol form has $\lambda_{max} = 244$ nm and $\varepsilon = 16000$.

From strength of 244 nm band, we can measure proportions of tautomers present in ethyl acetoacetate.

(7) Detection of impurities : The impurities present in organic compounds can easily be detected by UV absorption spectroscopy. The main reasons for the superiority of this method are :

(i) The bands due to impurities are very intense.

(ii) The organic compounds can be classified into saturated compounds having little absorption, while the unsaturated compounds have strong absorption bands.

Problem 10. ***Write a short note on Born-Oppenheimer approximation.***

The system of two protons and one electron presents a typical three-body problem, and no exact (analytic) solution is possible for the motions of three interacting bodies, either in classical or quantum mechanics.

An important approximate treatment, however, can be applied to this and other molecular problems that involve systems of nuclei and electrons. The masses of nuclei are some thousands of times the mass of an electron, and nuclear motions are slow and ponderous compared to those of electrons. The motions of nuclei as they vibrate in molecules are so slow compared to motions of the electrons that we can calculate the electronic states (wave functions and energy levels) *on the assumption that the nuclei are held in fixed positions.* This method was first used by Max Born and J. Robert Oppenheimer (1927) and is known as Born–Oppenheimer approximation. It has been basic to most quantum mechanical calculations of the properties of molecules.

As a result of the Born-Oppenheimer approximation, we can fix the positions of the nuclei in a molecule and then calculate the stationary-state wave functions for the electrons in this system of fixed nuclear charges. In the case of the H_2^+ system in fig. (9), the distance R is held constant, and only r_a and r_b are varied. Once this problem is solved, a new fixed value of R is taken, and the problem of the electronic motion solved for this new value. The internuclear distance R is thus a constant parameter in any one calculation.

When the calculations have been made for a number of values of R, the energy E (R) of the system can be plotted against R. The curve that results from the calculations for H_2^+ is shown in fig. (10). Such a plot is usually called the *potential-energy curve* for the diatomic molecule. The force between the nuclei is given by the

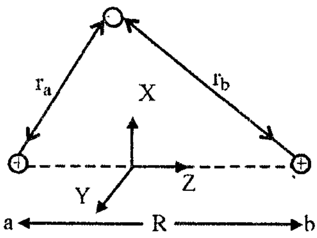


Fig. 9. Coordinates of H_2^+ at a particular internuclear distance, R

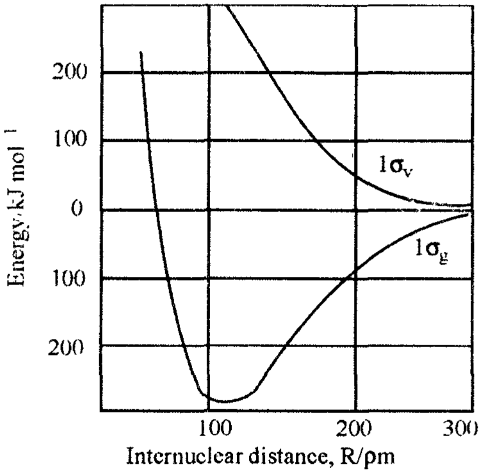


Fig. 10. Energy of H_2^+ as function of internuclear distance, *R*

derivative of this effective potential-energy function $E(R)$ at any separation R between the nuclei, $F = -(\partial E/\partial R)$. Note that the energy $E(R)$ contains the potential energy of internuclear repulsion and both the potential and kinetic energies of the rapidly moving electrons. The $E(R)$ is the effective potential energy for the vibrating motion of the nuclei. It is identical with the vibrational potential energy.

Problem 11. ***Derive an expression for the rotational energy of a diatomic molecule by assuming it to be a rigid rotator. Draw the rotational energy level diagram for such a molecule.***

On the basis of wave mechanics, it can be seen that if diatomic molecule is considered to be a rigid rotator, *i.e.*, like a rigid dumb bell joined along its line of centres by a bond equal in length to the distance r_0 between the two nuclei (Fig. 11), then the allowed rotational energies of the molecule around the axis passing through the centre of gravity and perpendicular to the line joining the nuclei are given by

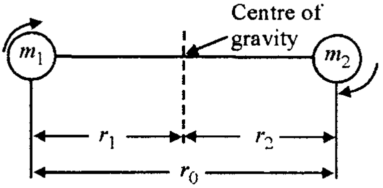


Fig. 11. Rigid rotator.

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

where J is the rotational quantum number. It can have values 0, 1, 2, 3 etc. The term I is the moment of inertia of the molecule about the axis of rotation, and is given by,

$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r_0^2 = \mu r_0^2$$

where m_1 and m_2 are the atomic masses of the two atoms of the diatomic molecule and μ is known as reduced mass, given by,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

[I] Expression For Rotational Energy

We know that the centre of gravity of a diatomic molecule is the point which satisfies the following condition (1)

$$m_1 r_1 = m_2 r_2 \qquad \dots (1)$$

The moment of inertia of the diatomic molecule is given by,

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \dots (2)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$= r_1 r_2 (m_1 + m_2) \qquad \ldots (3)$$

But $$r_1 + r_2 = r_0 \qquad \ldots (4)$$

∴ From equation (1), $m_1 r_1 = m_2 (r_0 - r_1)$

or $$m_1 r_1 = m_2 r_0 - m_2 r_1$$

or $$m_1 r_1 + m_2 r_1 = m_2 r_0$$

or $$(m_1 + m_2) r_1 = m_2 r_0$$

or $$r_1 = \frac{m_2 r_0}{m_1 + m_2} \qquad \ldots (5)$$

Similarly, $$r_2 = \frac{m_1 r_0}{m_1 + m_2} \qquad \ldots (6)$$

Substituting the values of r_1 and r_2 in equation (2), we get

$$l = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r_0^2 + \frac{m_1^2 m_2}{(m_1 + m_2)^2} r_0^2$$

$$= \frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)^2} r_0^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$$= \mu r_0^2 \qquad \left(\text{where } \mu = \frac{m_1 m_2}{m_1 + m_2} \right) \qquad \ldots (7)$$

Now, by definition, the angular momentum of a rotating molecule is given by

$$L = l\omega \qquad \ldots (8)$$

where ω is the angular velocity (just as linear momentum is given by the product of mass and velocity).

However, angular momentum is quantized whose values are given by

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} \qquad \ldots (9)$$

where $J = 0, 1, 2, 3 \ldots$, called the *rotational quantum numbers.*

Further the energy of a rotating molecule is given by

$$E = \frac{1}{2} I\omega^2$$

∴ The quantized value of the rotational energy will be given by

$$E_r = \frac{1}{2} I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \qquad \ldots (10)$$

Substituting the value of L from equation (9) in equation (10), we get

$$E_r = J\,(J+1)\,\frac{h^2}{4\pi^2} \times \frac{1}{2I}$$

or

$$E_r = \frac{h^2}{8\pi^2 I}\,J\,(J+1) \qquad \ldots (11)$$

Putting $J = 0, 1, 2, 3$ etc. in equation (11), pattern of the rotational energy levels obtained will be as shown in figure (10). It is clear that the spacing between the energy levels increases as J increases, because of the factor $J\,(J+1)$ in equation (11).

Problem 12. ***Give a qualitative description of a non-rigid rotor.***

The bonds in a diatomic molecule are supposed to be elastic to a certain extent. The elasticity in some molecules changes such as,

(i) An electric bond may have vibrational energy.

(ii) The quantities r and B change during a vibration.

When the spectrum of a non-rigid rotor is taken, the above two facts must be taken into consideration. For a non-rigid rotor, Schrodinger's wave equation provides the following rotational terms;

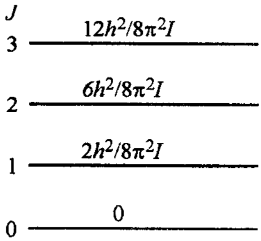


Fig. 12. Rotational energy levels of a diatomic molecule treating it as a rigid rotator.

$$E_j = \frac{h^2}{8\pi^2 I}\,J\,(J+1) - \frac{h^4}{32\,\pi^4\,I^2\,r^2 k}\,J^2\,(J+1)^2 \text{ joules}$$

or

$$E_i = \frac{E_j}{hc} = BJ\,(J+1) - DJ^2\,(J+1)^2 \text{ cm}^{-1}$$

where B is *rotational constant* which depends on the moment of inertia and rotational quantum number J. The value of B is given by, $B = h/8\pi^2 Ic$. The factor D is known as *centrifugal distortion constant* whose value is given by,

$$D = \frac{h^3}{32\pi^4\,I^2 r^2 kc}\text{ cm}^{-1}$$

where k is force constant and given by,

$$k = 4\pi^2\,\bar{\omega}^2\,c^2\mu$$

where ω is the vibrational frequency expressed in cm^{-1}.

From the defining equations of B and D, we can show that,

$$D = \frac{16\,B^3\,\pi^2 \mu c^2}{k} = \frac{4B^3}{\overline{\omega}^2} \qquad \text{... (1)}$$

It is generally found that vibrational frequencies are of the order of $10^3\ \text{cm}^{-1}$. The value of B is found to be of the order of $10\ \text{cm}^{-1}$. The value of D as given by equation (1), is of the order of $10^{-3}\ \text{cm}^{-1}$, which is very small as compared to that of B.

Problem 13. ***Derive an expression for the frequency and wave number of lines in the rotational spectrum.***

We know that the allowed rotational energies are given by the expression

$$E_r = \frac{h^2}{8\pi^2 I} J\,(J+1) \qquad \text{... (1)}$$

As $E = h\nu$, therefore, in terms of frequency, we can write

$$\nu = \frac{h}{8\pi^2 I} J\,(J+1) \qquad \text{... (2)}$$

Further we know that, $c = \nu\lambda = \nu/\bar{\nu}$ (because wave number $\bar{\nu} = 1/\lambda$). Therefore, in term of wave numbers, equation (2) can be written as

$$\bar{\nu} = \frac{h}{8\pi^2/c} J\,(J+1) \qquad \text{... (3)}$$

$$= BJ\,(J+1) \qquad \text{... (4)}$$

where $B = h/8\pi^2 Ic$ and is called *rotational constant.*

Putting $J = 0, 1, 2, 3$ etc. in equation (4), the wave numbers of the different rotational levels will be 0, $2B$, $6B$, $12B$, $20B$, $30B$ ...., and so on. When a transition takes place from a lower rotational level with rotational quantum number J to a higher rotational level with rotational quantum number J', the energy absorbed will be given by

$$\Delta E_r = E_r' - E_r \quad (\text{or } E_{J'} - E_J)$$

$$= \frac{h^2}{8\pi^2 I} J'\,(J'+1) - \frac{h^2}{8\pi^2 I} J\,(J+1)$$

$$= \frac{h^2}{8\pi^2 I} [J'\,(J'+1) - J\,(J+1)] \qquad \text{... (5)}$$

However, according to the rotational selection rules, only those rotational transitions are allowed for which $\Delta J = \pm 1$. Therefore, in

the present case $J' = J + 1$. Substituting this value in equation (5), we get

$$\Delta E_r = \frac{h^2}{8\pi^2 I}[(J+1)(J+2) - J(J+1)]$$

$$= \frac{h^2}{8\pi^2 I} 2(J+1) \qquad \dots (6)$$

To express in terms of wave numbers, we put

$$\Delta E_r = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$$

$$\therefore \qquad hc\bar{\nu} = \frac{h^2}{8\pi^2 I} \times 2(J+1)$$

or

$$\bar{\nu} = \frac{h}{8\pi^2 Ic} \times 2(J+1)$$

$$= 2B(J+1) \qquad \dots (7)$$

where $B = \dfrac{h}{8\pi^2 Ic}$ and is rotational constant. The value of $\bar{\nu}$ in equation (7) represents the wave numbers of the spectral lines which will be obtained as a result of the transitions between the rotational levels. Putting $J = 0, 1, 2, 3$ *etc.* (*i.e.*, for the transitions $J = 0$ to $J' = 1$; $J = 1$ to $J' = 2$ etc,) or in general from J to $J + 1$ (involving absorption of energy), the wave numbers of the lines obtained will be $2B$, $4B$, $6B$, $8B$, ..., and so on.

We find that the most important fact of the pure rotational spectrum is that every two successive lines have a constant difference of wave number equal to $2B$. This is known as **frequency separation** (or more strictly **wave number separation**). Thus, the various lines in the rotational spectra will be equally spaced as shown in figure (13).

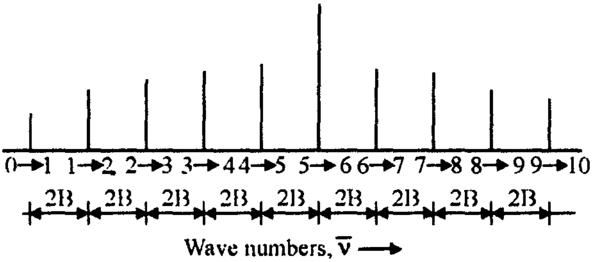


Fig. 13. Appearance of a rotational spectrum.

Any two successive lines will have the difference in wave number given by

$$\Delta\bar{\nu} = 2B = \frac{h}{4\pi^2 Ic}$$

Another important feature of spectra is that the intensities of different transitions are not equal. The intensities increase with increasing J, pass through a maximum and then decrease as J increases further.

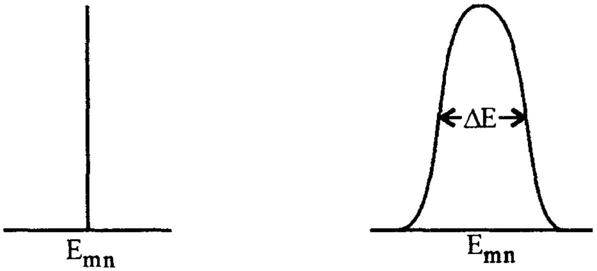
Problem 14. ***What are the selection rules for rotational and vibrational spectra?***

Atomic spectrum as well as molecular spectrum are obtained due to the transition taking place between energy levels. However, such transitions can occur only between definite energy levels and not between just any two energy levels. ***The restrictions thus applied on the transition are governed by certain rules which are called the selection rules.*** If the selection rules are followed, the transition can occur and it is called an **allowed transition.** If these are not followed, the transition cannot take place and it is called a **forbidden transition.** The selection rules to be followed depend upon the type of transition.

The selection rules are generally expressed in terms of changes in quantum numbers for the allowed transitions. For example, for the pure rotational transition, the selection rule is $\Delta J = \pm 1$, where J represents rotational quantum number ($\Delta J = +1$ corresponds to absorption and $\Delta J = -1$ corresponds to emission). Similarly, for pure vibrational transition, the selection rule is $\Delta v = \pm 1$, where v represents the vibrational quantum number.

Problem 15. ***Write a note on width and intensity of spectral lines.***

On analysing the spectrum of a molecule, the first thing we wish to know is how sharp and how intense (strong) is the spectral line. In other words, we are interested in the width and intensity of a spectral line. These two quantities are common in all types of spectroscopy. Fig. (14–a) exhibits a sharp spectral line having no width, while figure (14–b) exhibits a spectral line having a width ΔE at half height. It is always desired that the spectral lines were all very sharp and very intense. But in actual practice, this is not so.



(a) Sharp spectral line (b) Spectral line having a width

Fig. 14

Two factors are responsible for broadening of a spectral line, *viz.,* (i) The collision broadening and (ii) the Doppler broadening. The first factor is largely responsible for the width of spectral lines in the UV and visible regions. These transitions mostly occur between electrons in the outer shells in a molecule. When molecules in the liquid or gaseous phase collide with one another, they deform the charge clouds of the outer electrons, due to which the energy levels of these electrons are slightly perturbed. So, the spectral transitions between these perturbed energy levels are broadened.

The second factor, *i.e.,* Doppler broadening arises when the molecule under study has a velocity relative to the observer or observing instrument. This is generally seen in case with gaseous molecules, where the molecules are undergoing random motion. If the molecule is moving towards the measuring instrument with a velocity u, then the frequency ν of radiation seen by the molecule is given by

$$\nu' = \nu\left(1 + \frac{u}{c}\right) \qquad \text{... (1)}$$

where ν is the radiation frequency and c is the velocity of light. If on the contrary, the molecule is moving away from the measuring instrument, the frequency of radiation seen by the molecule is given by

$$\nu' = \nu\left(1 - \frac{u}{c}\right) \qquad \text{... (2)}$$

On rearranging equation (1), we get

$$\frac{(\nu - \nu')}{\nu} = \frac{\Delta\nu}{\nu} = -\frac{u}{c} \qquad \text{... (3)}$$

Simiarly, rearranging equation (2), we get

$$\frac{(\nu - \nu')}{\nu} = \frac{\Delta\nu}{\nu} = \frac{u}{c} \qquad \ldots (4)$$

The quantity $\Delta\nu$ is known as *Doppler broadening*. It is seen that $\frac{\Delta\nu}{\nu}$ is proportional to $T^{1/2}$. So, Doppler broadening can be reduced (and spectral lines of maximum sharpnesss can be obtained) by working with cold gaseous examples.

Problem 16. ***Derive an expression for the spectral intensities of rotational lines.***

It is expected that the relative intensities of the spectral lines will depend upon the relative populations of the energy levels. We can show that *greater the population of an energy level, greater is the number of molecules that can be promoted to the next higher level and hence greater is the intensity of absorption.* The population of a rotational energy level with quantum number J relative to that of the ground level for which $J = 0$ is given by Boltzmann's distribution law for which the equation is given by,

$$\frac{N_J}{N_0} = e^{-E_J/kT} \qquad \ldots (1)$$

However, rotational energy levels are degenerate and the degeneracy of any rotational level with quantum number J is given by

$$g_J = 2J + 1 \qquad \ldots (2)$$

If we take into account the degeneracy factor, equation (1) should be replaced by

$$\frac{N_J}{N_0} = g_j\, e^{-E_J/kT} \qquad \ldots (3)$$

From equations (2) and (3), we can write

$$\frac{N_J}{N_0} = (2J + 1)\, e^{-E_J/kT} \qquad \ldots (4)$$

We know that,

$$\text{Intensity} \propto \frac{N_J}{N_0} = (2J + 1)\, e^{-E_J/kT}$$

Putting $E_J = h\nu = h\frac{c}{\lambda} = hc\bar{\nu} = hc\,BJ\,(J + 1)$, we get

$$\frac{N_J}{N_0} = (2J + 1)\, e^{-hcBJ\,(J + 1)/kT}$$

As J increases, the first factor *viz.*, $(2J + 1)$ increases, whereas the exponential factor decreases slowly in the beginning and then rapidly as the values of J become higher and higher. So, the plot of N_J/N_0 (Y-axis) versus J (X-axis) for a rigid diatomic molecule is obtained as shown in figure (12).

The graph (Fig. 15) clearly shows that relative population and hence the intensity of transitions first increases, reaches a maximum value and then decreases.

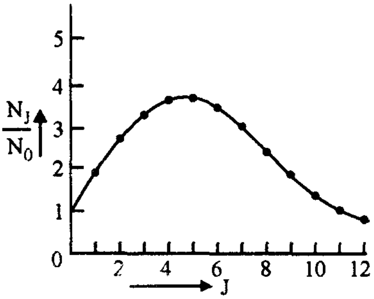


Fig.15. Plot of relative population of rotational energy levels versus rotational quantum number.

Problem 17. ***How will you determine bond length of a molecule from its rotational spectra? How is the rotational spectrum of a substance obtained experimentally?***

(Meerut 2005)

By determining the frequency separation, $\Delta\bar{\nu}$, it is possible to calculate the moment of inertia I of the molecule, using equation $B = h/8\pi^2 Ic$. Then knowing the masses of the atoms present in the diatomic molecule, it is possible to calculate the distance between the atoms, r_0 (*i.e.*, internuclear distance or bond length) with the help of the equation

$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r_0^2$$

The source of radiations is a special type of electronic oscillator (called klystron). It produces radiations of frequency corresponding to wavelength range of 0.1 to a few hundred centimetres. The energies corresponding the these wavelengths are the same as needed for rotational transitions. The method consists in passing the monochromatic energy of the microwaves through the gaseous sample of the substance under study and measuring the intensity of the transmitted radiation. By varying the frequency of the oscillator and observing the intensity of the transmitted beams, the frequencies at which absorption takes place can be determined from the plot of transmitted intensity versus frequency.

Problem 18. ***(a) What type of molecules give rotational spectra? State which of the following molecules give rotational spectra ?***

H_2, HCl, CH_4, CH_3Cl, CO, N_2, Cl_2 and O_2 ?

(b) Why H_2, N_2, O_2 and Cl_2 do not show rotational spectrum? **(Meerut 2007, 06)**

The condition for obtaining a pure rotational spectrum is that the molecule must have a permanent dipole moment so that it can interact with the electromagnetic radiation and absorb or emit a photon. Thus, *pre rotational spectrum is given only by polar molecules*. Consequently, homonuclear diatomic molecules (like H_2, N_2 etc.) and symmetrical linear molecules like CO_2 (or symmetrical molecules like C_6H_6) do not give rotational spectra. Thus, polar molecules like H_2O, NO, N_2O etc., give pure rotational spectra.

Out of the given molecules HCl, CH_3Cl and CO possess a permanent dipole moment and will give rotational spectra. H_2, CH_4, N_2, Cl_2 and O_2 being non-polar will not show rotational spectra.

Problem 19. ***Write a short note on isotope effect.***

We know the relationship between nuclear mass and the frequency of vibration. If we assume, as is generally possible, that the force constants are unchanged by isotope substitution, the shift in observed frequency can be mainly attributed to mass effects. Qualitatively, this shift will help in the assignment of frequencies simply by observing what bands are altered and to what extent they are altered by isotopic substitution. Vibrational modes which largely involve the substituted species, *i.e.*, the species having a large amplitude in the normal vibrational mode, will be expected to have appreciable shifts in frequency. The larger the mass difference, the larger the frequency difference and thus deuterium substitution, for example, gives a particularly large effect because of the large difference in relative mass. In the simple case of diatomic molecules, such as HCl and DCl, the observed frequencies are approximately 2990 and 2091 cm^{-1}, respectively. Hence, the ratio 2091/2990 is 0.70 and ratio predicted is $\sqrt{\mu/\mu'}$, where μ and μ' are the reduced masses of HCl and DCl. The predicted value is 0.72 and is in close agreement.

NUMERICAL PROBLEMS

Problem 1. ***What is the moment of inertia of a diatomic molecule whose internuclear distance is* 150 pm *and the reduced mass is* 1.5×10^{-27} kg?**

Sol. The moment of inertia I of a diatomic molecule is given by the relation

$$I = \frac{m_1 m_2}{m_1 + m_2} \cdot r_0^2$$

where $\frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass and r_0 is the internuclear distance.

In S.I. units, reduce mass = 1.5×10^{-27} kg

and $r_0 = 150 \text{ pm} = 150 \times 10^{-12}$ m

$$\therefore \quad I = 1.5 \times 10^{-27} \times (150 \times 10^{-12})^2 \text{ kg m}^2$$

$$= 1.5 \times 150 \times 150 \times 10^{-27} \times 10^{-24}$$

$$= 33750 \times 10^{-51} = \mathbf{3.375 \times 10^{-47} \text{ kg m}^2}$$

Problem 2. ***The far infrared spectrum of HI consists of a series of equally spaced lines with*** $\Delta\bar{\nu} = 12.8$ **cm**$^{-1}$***. What is the (a) moment of inertia and (b) internuclear distance ?***

Sol. (1) Here we are given

$$\Delta\bar{\nu} = 12.8 \text{ cm}^{-1}$$

$$I = \frac{h}{4\pi^2 c \cdot \Delta\bar{\nu}} = \frac{6.62 \times 10^{-27}}{4 \times (3.14)^2 \times (3 \times 10^{10}) (12.8)}$$

$$= \mathbf{4.36 \times 10^{-40} \text{ g cm}^2}$$

(2) $$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r_0^2$$

$$m_1 \text{ (for H-atom)} = \frac{1.008}{6.022 \times 10^{23}} \text{ g} = 1.6739 \times 10^{-24} \text{ g}$$

$$m_2 \text{ (for I-atom)} = \frac{127}{6.022 \times 10^{23}} \text{ g} = 2.1089 \times 10^{-22} \text{ g}$$

$$\therefore \quad r_0^2 = \left(\frac{m_1 + m_2}{m_1 m_2}\right) \times I$$

$$= \frac{1.6739 \times 10^{-24} + 2.1089 \times 10^{-22}}{1.6739 \times 10^{-24} \times 2.1089 \times 10^{-22}} \times 4.36 \times 10^{-40}$$

$$= \frac{(1.6739 + 210.89) \times 10^{-24} \times 4.36 \times 10^{-40}}{1.6739 \times 2.1089 \times 10^{-46}}$$

$$= 2.6254 \times 10^{-16} \text{ cm}^2$$

$$\therefore \quad r_0 = \mathbf{1.62 \times 10^{-8} = 1.62 \text{ Å}}$$

In terms of S.I. units, we can calculate the values of I and r_0 as follows

(1) $\Delta \bar{v} = 12.8 \text{ cm}^{-1} = 1280 \text{ m}^{-1}$

$$\therefore \quad I = \frac{h}{4\pi^2 c \,.\, \Delta \bar{v}} = \frac{6.62 \times 10^{-34}}{4 \times (3.14)^2 \times (3 \times 10^8) \times 1280}$$

$$= \mathbf{4.36 \times 10^{-47} \ kg\ m^2}$$

(b) $m_1 = 1.6739 \times 10^{-27}$ kg

$m_2 = 2.1089 \times 10^{-25}$ kg

$$r_0^2 = \left(\frac{m_1 + m_2}{m_1 m_2}\right) \times I$$

$$= \frac{1.6739 \times 10^{-27} + 2.1089 \times 10^{-25}}{1.6739 \times 10^{-27} \times 2.1089 \times 10^{-25}} \times 4.36 \times 10^{-47}$$

$$= 2.6254 \times 10^{-20}$$

$$\therefore \quad r_0 = 1.62 \times 10^{-10} \text{ m} = \mathbf{0.162\ nm.}$$

Problem 3. ***Calculate the frequency, if*** $c = 3 \times 10^{10}$ ***cm/sec and*** $\lambda = 4000$ **Å.** **(Meerut 2007)**

Sol. We know that, $\lambda = \frac{c}{v}$, where v = frequency.

or $$v = \frac{c}{\lambda} = \frac{3 \times 10 \text{ cm sec}^{-1}}{4000 \times 10^{-8} \text{ cm}}$$

or $$v = \mathbf{7.5 \times 10^{14}\ sec^{-1}}$$

EXERCISE

[I] Short Answer Type Questions

1. Explain the different regions of spectrum.
   [For answer, please see problem 2]
2. Mention the electromagnetic radiations.
   [For answer, please see problem 1]
3. Write a short note on Born-Oppenheimer approximation.
   [For answer, please see problem 10]
4. What are the basic features of different spectrometers ?
   [For answer, please see problem 3]
5. Mention important applications of ultraviolet spectroscopy.
   [For answer, please see problem 9]
6. Describe the qualitative description of a non-rigid rotor.
   [For answer, please see problem 12]
7. Write a note on width and intensity of spectral lines.
   [For answer, please see problem 15]

8. How will you determine the bond bength of a molecule from its rotational spectrum ?
   [For answer, please see problem 17]
9. Derive an expression for the frequency of spectral lines in rotational spectrum.
   [For answer, please see problem 14]

[II] Very Short Answer Type Questions

1. Relate the units micron, angstrom and nanometre.
   [For answer, please see problem 1] **(Meerut 2007, 06)**
2. Define the term spectroscopy.
   [For answer, please see problem 1]
3. Give the relation between wavelength and frequency of a radiation.
   [For answer, please see problem 1]
4. Define wave number. (See Problem 1)
5. Define absorption spectrum.
   [For answer, please see problem 2]
6. Define emission spectrum.
   [For answer, please see problem 2]
7. Explain the term chromophore. **(Meerut 2005)**
   [For answer, please see problem 6]
8. Explain the term auxochrome. **(Meerut 2005)**
   [For answer, please see problem 6]
9. Mention the selection rules for rotational spectra.
   [For answer, please see problem 14]
10. What are the selection rules for vibrational spectra?
    [For answer, please see problem 14]
11. Why H_2, N_2, O_2 and Cl_2 do not show rotational spectrum?
    [For answer, please see problem 18] **(Meerut 2007, 06)**
12. Define intensity of a spectral line ?
    [For answer, please see problem 15]
13. Calculate the frequency if $c = 3 \times 10^{10}$ cm sec^{-1} and $\lambda = 4000\text{Å}$.
    [For answer, please see numerical problem 3] **(Meerut 2007)**
14. Identify the spectra which correspond to the following frequency/wave length :
    (a) 15,000 cm^{-1} (b) 50,000 cm^{-1}
    [**Ans.** (a) Visible (b) UV]
15. Write a short note on isotope effect.
    [For answer, please see problem 19]

❑❑❑

UNIT-2

SPECTROSCOPY, VIBRATIONAL AND ELECTRONIC SPECTRUM

Infrared spectrum : Energy levels of simple harmonic oscillator, selection rules, pure vibrational spectrum, intensity, determination of force constant and qualitative relation of force constant and bond energies, effect of an harmonic motion and isotope on the spectrum, idea of vibrational frequencies of different functional groups.

Raman spectrum : Concept of polarizability, pure rotational and pure vibrational Raman spectra of diatomic molecules, selection rules.

Electronic spectrum : Concept of potential energy curves for bonding and antibonding molecular orbitals, qualitative description of selection rules and Franck-Condon principle.

Qualitative description of σ, π- and n-M.O., their energy levels and the respective transitions.

PROBLEMS

Problem 1. ***What is infrared spectroscopy? Mention the units used and ranges in infrared radiations.***

[I] Introduction

Infrared spectroscopy is one of the most powerful analytical techniques which gives us the possibility of chemical identification. Radiations in the infrared region from about 800 to 20,000 nm are not energetic enough to cause electronic excitations in most organic molecules. IR radiations cause stretching and bending of organic bonds. In all organic molecules, the bonds, which join different atoms, can stretch and bend and all of them absorb infrared radiations. After absorption of IR radiations, the molecules thus give rise to close packed absorption bands known as *infrared absorption spectrum*. This may extend over a wide wavelength range. A number of bands may be present in infrared spectrum corresponding to the characteristic functional groups and bonds present in the substance. There, we say that *infrared spectrum of a chemical compound is a finger print for its identification.*

[II] Units Used and Range in Infrared Radiation

Infrared spectra are generally expressed in terms of the frequencies of radiations absorbed rather than wavelengths. This is due to the reason that frequency is directly proportional to the energy of the radiation, whereas wavelength is inversely proportional to energy. The most common unit used in infrared study is wave number $\bar{\nu}$, which shows the number of vibrations of radiation per centimetre (cm^{-1}). Wavelengths in μm can be converted into wave numbers, according to the relation

$$\bar{\nu} = \frac{10^4}{\lambda} \qquad (\because\ 1\,\mu = 10^{-6}\text{ m} = 10^{-4}\text{ cm})$$

The infrared radiation lies between the visible microwave regions of the electromagnetic spectrum. This region may be divided into the following three types.

(i) *Near infrared region* : It is the region which extends from 0.8 to 2.5 μm (12500 to 4000 cm^{-1}). It is also known as ***vibration-rotation region.***

(ii) *Far infrared region* : It is the region which extends from 15 to 200 μm (667 to 50 cm^{-1}). It is also known as ***rotation region.***

(iii) *Ordinary infrared region* : It is the region which extends from 2.5 to 1.5 μm (4000 to 667 cm^{-1}).

Problem 2. *Discuss the molecular vibrations and origin of infrared spectrum.*

The atoms in a molecule are always in motion, which may be of different types. Consider a simple diatomic molecule A-B. The only vibrations which can occur in such a molecule are the compression or extension along the A-B bond. This may be compared to the compression or stretching of a coiled spring as shown in figure (1). This type of vibrational movement is referred to as *bond stretching, i.e.,* in these vibrations the distance between two atoms increases or decreases, but the atoms remain in the same bond axis. Such a mode of vibration does not cause any dipole change in the symmetrical molecule, *e.g.*, O =C= O and, therefore, it is not ***infrared active vibration.***

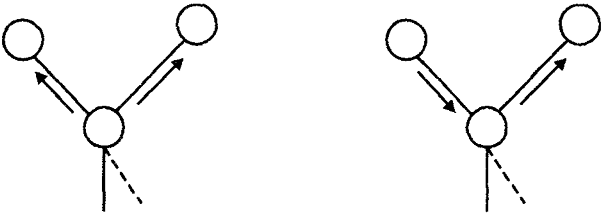

(Symmetric) (Asymmetric)

Fig. 1. Kinds of stretching vibrations.

When the stretching and compression occur in a symmetrical fashion, we call it ***symmetric stretching.*** But when one bond is compressing, while the other is stretching, then it is known as ***asymmetric stretching.***

In bending or deformation vibrations, atoms move in and out of the bond axis plane. So, these vibrations involve change in bond angle or a movement of a group of atoms with respect to the rest of the molecule, without movement of atom in the group with respect to one another. Therefore, the bending mode of vibrations involves oscillations of atom perpendicular to its chemical bond. The bending modes are of four types :

(i) Rocking : In this mode of vibration, the two atoms joining a central atom, move back and forth in the plane of the molecule.

(ii) Scissoring : In this deformation, the two atoms, joined to a central atom, move towards and away from each other. In this mode, the bond angle changes.

(iii) Twisting : In this deformation, the structural unit rotate about the bond, which joins it to the rest of the molecule.

(iv) Wagging : In this kind of vibration, the structural unit moves back and forth, out of the plane of molecule.

Now we will consider vibrational modes in some particular cases.

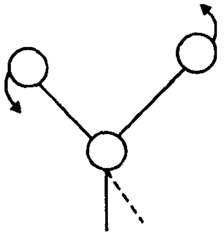


Fig. 2. Rocking mode of vibration.

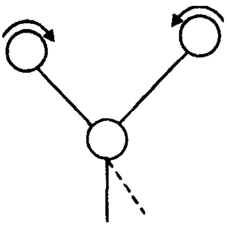


Fig. 3. Scissoring mode of vibration.

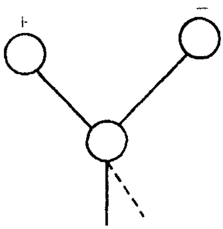


Fig. 4. Twisting mode of vibration. + or − sign signifies vibrations perpendicular to the plane of paper.

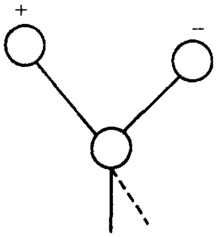


Fig. 5. Wagging mode of vibration. The + sign means vibrations perpendicular to the plane of paper.

[I] Diatomic Molecules

The diatomic molecule is invariably linear. Therefore, the number of modes of vibration

$$= 3n - 5$$
$$= 3 \times 2 - 5 = 1.$$

Thus, there can be only one mode of vibration. In case of homo-nuclear diatomic molecules, because of their zero dipole moment for all bond lengths, no vibrational energy exchange would be possible, and as a result, such molecules would be *infrared inactive*.

In any hetero-nuclear diatomic molecule, *e.g.*, HCl, NO, CO, etc. the variation in dipole moment due to fluctuations in the bond length, would make these molecules *infrared active.*

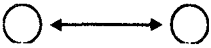


Fig. 6. Stretching in diatomic molecule.

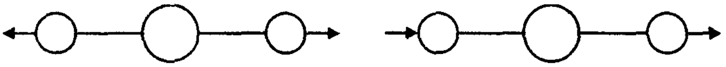
[II] Polyatomic Molecules

There are some polyatomic molecules which do not possess a permanent dipole, but because of certain modes of vibrations, develop a fluctuating dipole and respond to the infrared region of electromagnetic radiation. Now consider some *linear* and *bent triatomic molecules.*

(a) Linear triatomic molecule, *e.g.*, CO_2 : It has the following vibrational modes.

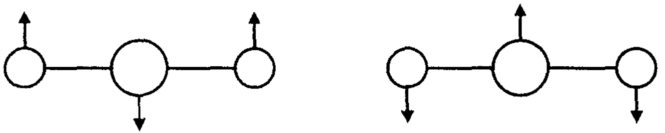
$$\text{Number of vibrational modes} = (3n - 5)$$
$$= 3 \times 3 - 5 = 4.$$

Therefore, allowed modes of vibrations are 4. These are as shown in fig. (7) :



(i) Symmetrical stretching
ν = 1340 cm^{-1} I.R inactive

(ii) Asymmetrical stretching
ν = 2350 cm^{-1} I.R. active



(iii) Bending, ν = 666 cm^{-1}

(iv) Bending, ν = 666 cm^{-1}

Fig. 7. Stretching in a linear triatomic molecule of CO_2.

Thus, we see that the fourth mode of vibration is identical with the third one. The frequencies associated with the fourth and third are the same. Such motions, which are identical in all respects, except direction, are called ***degenerates***. So, in case of CO_2, third mode is doubly degenerate, *i.e.*, the fourth mode is another bending type, identical in character and frequencies to the third (ν = 666 cm^{-1}).

Problem 3. ***Discuss the principle and different parts of an infrared spectrophotometer.***

The instrument used for recording infrared spectra is called ***infrared spectrometer or infrared spectrophotometer.*** Most of the instruments have a range of 2μ to 15μ (5000 – 667 cm^{-1}). The general parts of a spectrophotometer and their functions are mentioned below :

(a) Radiation source : The source of infrared radiation is primarily an incandescent solid material, which follows the characteristics of a black body radiator. The tungsten filament lamp is the usual source of near infrared region. It is maintained at red hot by means of an electric current. The most recent source is the invention of K.H. Opperman (Fig. 8). It operates at 2.8 volts and 30 watts. It provides radiant infrared energy from 2.5 μ (4000 cm^{-1}) to 25 μ (400 cm^{-1}).

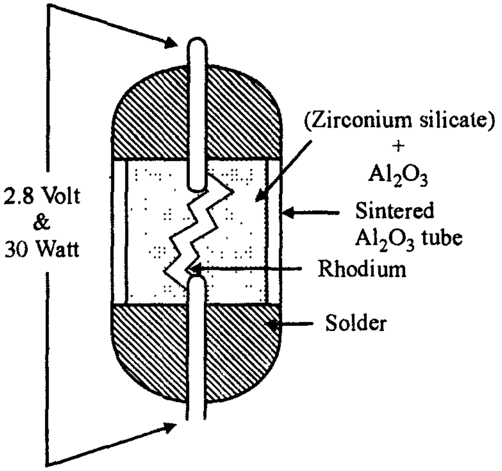


Fig. 8. Source developed by K.H. Opperman.

(b) Infrared monochromator : Prisms and gratings are generally used as monochromators. A combination of prism and grating is also used for this purpose. The most common prism material used is NaCl (rock salt) for the region 2.5 to 15.4 μ (4000 – 650 cm^{-1}). KBr (1000-4000 cm^{-1}) and CsI (1000-260 cm^{-1}) are also commonly used.

(c) Cell compartment : It is the portion where the cells in which the sample under examination is placed. They are usually made of rock salt (NaCl) or other similar substances.

Sampling : It is important that substances are sampled suitably for infrared spectral studies :

(i) Gaseous substances : Gaseous substances are examined as such in the apparatus.

(ii) Liquid substances : Liquid substances are examined by placing a thin film between the rock salt plates of a liquid cell. A drop of the liquid substance is put on a rock salt plate of a liquid cell and the other plate of the cell is put on it so that the liquid forms a thin film between the two plates.

(iii) Solid substances : Solid substances can be examined in the form of a potassium bromide disc (or pellet) or a Nujol mull or a solution in a suitable solvent.

(a) KBr pellet or disc : The solid is ground with 10-100 times its bulk of pure KBr and the mixture so obtained is passed into a disc using a special mould through a hydraulic press. The pellet must be transparent.

(b) Nujol mull : Nujol is a highly purified liquid fraction petroleum known as liquid paraffin. The substance (1 mg) is finely ground with *nujol* in a small agate pestle mortar to form a translucent mull of the substance. A drop or two of this mull is taken as the liquid sample.

(c) Solution : The given compound is dissolved to give 1-5% solution in CCl_4, carbon disulphide or chloroform free from alcohol. This solution is introduced into a special cell, 0.1 to 1 mm. thick, made of sodium chloride. A second cell of equal thickness, but containing pure solvent, is placed in path of other beam of spectrometer in order that solvent absorptions should be balanced. Spectra taken in such dilute solution in non-polar solvents are generally more desirable since intramolecular forces which are strong in crystalline state are reduced to minimum error. On the other hand, it is found that many compounds which are not soluble in non-polar solvents absorb in infrared region. In this case, where solvent absorption exceeds 65% of incident light, the spectra cannot be taken, while in case of CCl_4 or $CHCl_3$ the absorption takes place above 65% of incident light.

[I] Principle of Infrared Spectrometer

The flow sheet diagram of the infrared spectrometer is shown in figure (9). The beam of infrared radiation from the source S is allowed to pass by means of lens L through a narrow slit T. This beam is then focussed by means of a mirror M on the grating G, which is provided with a rotating device. The radiations of a desired wavelength emerge from G. Such radiations are allowed to pass through a cell B, containing the solution under examination and from there to the detector-cum-indicator R. The intensity of the thermo-electric current, which is a measure of the intensity of

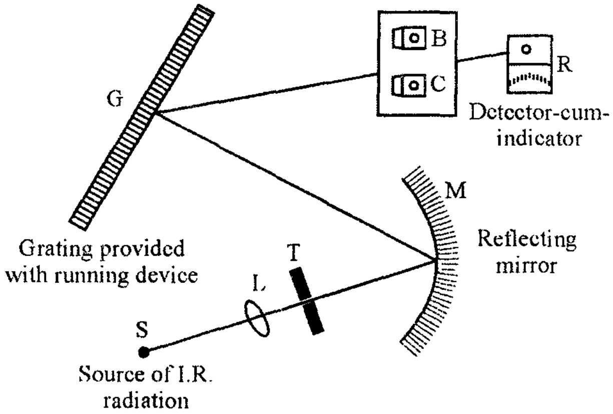


Fig. 9. Flow sheet diagram of I.R. spectrometer.

radiation, is recorded. The cell B is then replaced by a cell C containing pure solvent and again the intensity of radiation is recorded as before. If I and I_0 reprsent the intensity of radiation when the radiation passes through the solution and intensity of the same radiation when it passes through the solvent, then

$$I / I_0 = \text{Transmittance or transmittancy.}$$

The transmittance is determined at different wavelengths and thus infrared spectra is obtained.

The frequency of a given stretching vibration in an infrared spectrum can be related to two factors, namely (i) the masses of the bonded atoms–light atoms vibrate at higher frequencies than heavier ones-and (ii) the relative stiffness of the bond. Triple bonds are stiffer (and vibrate at higher frequencies) than double bonds and double bonds are stiffer (and vibrate at higher frequencies) than single bonds. We can see some of the effects in table 1. Notice that stretching frequencies of groups involving hydrogen (a light atom) such as C—H, N—H and O—H all occur at relatively high frequencies.

Table 1.

Group	Bond	Frequency range (cm^{-1})
Alkyl	C—H	2853–2972
Alcohol	O—H	3590–3650
Amine	N—H	3300–3500

It is clear from table 2 that triple bonds vibrate at higher frequencies than double bonds.

Table 2.

Bond	Frequency range (cm^{-1})
$C \equiv C$	2100–2260
$C \equiv N$	2220–2280
$C = C$	1620–1680
$C = O$	1630–1780

The infrared spectra of even relatively simple compounds contain many absorption peaks. Not all molecular vibrations result in the absorption of infrared energy. **In order for a vibration to occur with the absorption of infrared energy, the dipole moment of the molecule must change as the vibration occurs.** Thus, when the four hydrogen atoms of methane vibrate symmetrically, methane does not absorb infrared energy. Symmetrical vibrations of the carbon-carbon double and triple bonds of ethene and ethyne do not result in the absorption of infrared radiation, either.

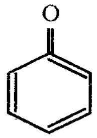
[II] Characteristics of Infrared Spectrum

Maximal absorption of an infrared radiation of a frequency characteristic of a bond or group would show the presence of that particular bond or group in the substance. In case the compound does not absorb maximally that particular radiation, it would mean that the particular bond or group is absent. So, we get characteristic infrared bands for different groups or bonds, as shown in table 3. It gives only the ranges of different bands. The exact location of characteristic band depends on several factors like structural environment of that bond or group in a specific molecule.

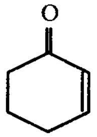
A strong bond ~ 1700 cm^{-1} indicates the presence of a carbonyl group, but these are characteristic shifts in the position of the carbonyl bond depending on the structural environment as shown below.

$CH_3COCH_2CH_3$
Methyl ethyl ketone (1710 cm^{-1})

$CH_3COCH = CH_2$
Methyl vinyl ketone (1680 cm^{-1})



Cyclohexanone (1710 cm^{-1})



2-Cyclohexenone (1680^{-1})

Table 3 : Characteristic infrared absorptions of groups

	Group		Frequency Range cm^{-1}	Intensity*
A.	**Alkyl**			
	C—H (stretching)		2853-2962	(m-s)
	Isopropyl, —$CH(CH_3)_2$		1380-1385	(s)
		and	1365-1370	(s)
	tert-Butyl, —$C(CH_3)_2$		1385-1395	(m)
		and	~ 1365	(s)
B.	**Alkenyl**			
	C—H (stretching)		3010-3095	(m)
	C= C (stretching)		1620-1680	(v)
	$R—CH = CH_2$ (Out of plane C–H bending)		985-1000	(s)
		and	905-920	(s)
	$R_2C = CHR$		880-900	(s)
	cis-RCH = CHR		675-730	(s)
	trans-RCH = CHR		960-975	(s)
C.	**Alkynyl**			
	≡ C—H (stretching)		~ 3300	(s)
	≡ C (stretching)		2100-2260	(v)
D.	**Aromatic**			
	Ar—H (stretching)		~ 3030	(v)
	Aromatic substitution type			
	(C—H out-of-plane bendings)			
	Monosubstituted		690-710	(very s)
		and	730-770	(very s)
	o Disubstituted		735-770	(s)
	m Disubstituted		680-725	(s)
		and	750-810	(very s)
	p Disubstituted		800-860	(very s)
E.	**Alcohols, Phenols and Carboxylic Acids**			
	O—H (stretching)			

	Alcohols, phenols (dilute solutions)	3590-3650	(sharp, v)
	Alcohols, phenols (hydrogen bonded)	3200-3550	(broad, s)
	Caroxylic acids (hydrogen bonded)	2500-3000	(broad, v)
F.	**Aldehydes, Ketones, Esters and Carboxylic acids**		
	C = O (stretching)	1630-1780	(s)
	Aldehydes	1690-1740	(s)
	Ketones	1680-1750	(s)
	Esters	1735-1750	(s)
	Carboxylic acids	1710-1780	(s)
	Amides	1630-1690	(s)
G.	**Amines**		
	N—H	3300-3500	(m)
H.	**Nitriles**		
	C≡N	2220-2260	(m)

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*Abbreviations : s = strong, m = medium, w = weak, v = variable,
~ = approximately.

Vibrational absorption may occur outside the region measured by a particular infrared spectrophotometer and vibrational absorptions may occur so closely together that peaks fall on top of peaks.

Other factors bring about even more combination peaks. Overtones (harmonics) of fundamental absorption bands may be seen in infrared spectra even though these overtones occur with greatly reduced intensity. Bands called combination bands and difference bands also appear in infrared spectra.

Because infrared spectra contain so many peaks, the possibility that two different compounds will have the same infrared spectrum is exceedingly small. It is because of this that an infrared spectrum has been called the "fingerprint" of a molecule. Thus, with organic compounds, if two pure samples give different infrared spectra, one can be certain that they are different compounds. If they give the same infrared spectrum then they are the same compounds.

Problem 4. ***Mention some important applications of infrared spectroscopy.*** **(Meerut 2006)**

Some important applications of infrared spectroscopy are as follows :

(1) **Qualitative analysis** : The qualitative analysis can easily be done by comparing the spectrum of unknown sample with the standard one.

(2) **Quantitative analysis** : The quantitative determination is based on the determination of concentration of one of functional groups of compound being estimated. Suppose there is a mixture of hexane and hexanol and then the concentration of hexanol can be determined by measuring the absorption of OH bond. The following formula is used for calculating the concentration

$$A = -\log I/I_0 = abc$$

where, A = absorbance,

I = intensity of radiation after leaving the sample,

I_0 = intensity of radiation before entering the sample.

a = absorptivity of cell (It is a property of molecular species being transmitted)

b = initial path length of sample cell, and

c = concentration of solution.

If a and b are constants then

$$A \propto c.$$

Hence, c can be measured by knowing A.

The different values of A are plotted against respective concentrations to get calibration curve from which the concentration of unknown solution is evaluated.

(3) **Determination of purity** : As impurity reduces the sharpness of individual bands and causes appearance of extra bands and blurring of spectrum. Hence purity can easily be estimated.

(4) **Presence of water in a sample** : If sample contains water, it gives bands at 3600 to 200 cm^{-1} region, in 1650^{-1}cm region and in 600-300 cm^{-1} region. If anyhow, water is coordinated to a metal ion, an additional band can be seen in the range 880-650 cm^{-1} region.

(5) **Calculation of force constant** : Taking a simple case where a diatomic molecule may be considered as a simple harmonic oscillator, *i.e.*, an oscillator in which the restoring force (F) is

directly proportional to the displacement, in accordance with Hooke's law, we have

$$F = -kx \qquad \ldots (1)$$

where x is the displacement and is equal to the distance (R) to which the atoms have been stretched minus equilibrium distance (R_e) between the atoms *i.e.*, $x = R — R_e$. The factor k in equation (1) is called force constant. So, if $x = 1$ cm, $k = -F$. Therefore *force constant may be defined as the restoring force per unit displacement (or per cm) of a harmonic oscillator.* It is found to be related to the equilibrium vibrational frequency ω_e according to the equation,

$$\omega_e = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad \ldots (2)$$

where μ is the reduced mass of the system.

To calculate k, equation (2) can be rewritten as follows :

$$k = 4\pi^2\, \omega_e^2\, \mu$$

or

$$k = 4\pi^2\, \omega_e^2\, \frac{m_1 m_2}{m_1 + m_2} \qquad \ldots (3)$$

where m_1 and m_2 are the masses of the oscillating atoms.

Thus, knowing vibration frequency ω_e and the masses of the atoms of the diatomic molecule, the force constant k can be calculated. Note that ω_e is in s^{-1}.

It is found that force constant, increases almost directly with the multiplicity of the bond, as is clear from the following examples.

Bond	C—C	C=C	C≡C
Force constant (dyne/cm)	4.6×10^5	9.5×10^5	15.8×10^5

Thus, multiplicity of the bond can be predicted from the value of the force constant. For example, the force constant for C≡O in carbon monoxide is 18.6×10^5 dynes/cm, whereas the force constant for C=O in carbon dioxide is 15.2×10^5 dynes/cm. This result confirms that CO_2 has resonating structures containing both carbon, oxygen double and triple bonds. So, the struture of CO_2 can be depicted as :

$$O^+—C\equiv O^- \longleftrightarrow O=C=O \longleftrightarrow O^-\equiv C—O^+$$

(6) Shape and symmetry of a molecule : Infrared spectroscopy has been proved very successful in deducing the shape or symmetry of molecules. For example, if NO_2 is linear, only two bands will be active in infrared spectrum and if bent then three bands will be found as in H_2O.

(7) In the study of reaction kinetics : The technique is helpful in the study of reaction kinetics as intermediate compounds can easily be detected and estimated, *e.g.*, progress of oxidation of a secondary alcohol to ketone is studied by getting infrared spectra of test portions at different times. In this case, we expect disappearance of O—H stretching ~ 2.8 μm (~ 3570 cm^{-1}) and appearance of C=O stretching ~ 5.8 μm (~ 1725 cm^{-1}).

(8) Calculation of moment of inertia and bond length :

The value of B is given by

$$B = \frac{h}{8\pi^2 Ic}$$

$$\therefore \quad \text{Frequency separation, } \Delta\bar{\nu} = 2B = \frac{h}{4\pi^2 Ic}$$

Thus, knowing the frequency separation, the moment of inertia and hence the internuclear distance *i.e.*, bond length of a diatomic molecule can calculated.

(9) Identification of functional groups : Tables 4 and 5 are given below from which different functional groups can easily be detected.

Table 4 : Saturated C—H and C—C bonds

	Group	Band, cm^{-1}	Remarks
(i)	$>CH_2$ $—CH_2$	2969-2850 (s)	Two or three bands usually
(ii)	$\geq CH$	2890-2880 (w)	—C—H stretching
(iii)	$>CH_2$ $—CH_3$	1470-1430 (m)	—C—H deformations
(iv)	$—CH_3$	1390-1370 (m)	$—CH_3$ symmetrical deformation
(v)	$>CH_2$	~ 720 (w)	$>CH_2$ rocking

(10) The characteristic series of bands produced by —O—H in alcohols and phenols are given in table 5.

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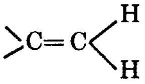
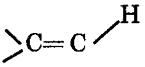
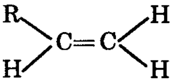
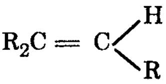
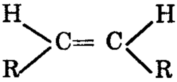
*All bands are strong unless written otherwise in parentheses. The abberviations used to indicate intensities are : *m* (moderate). *w* (weak) and v (variable).

It is also seen that if hydrogen bond is stronger, then there will be longer O—H bond. Besides this, if the vibration frequency is lower, we will get broader and more intense absorption bands. The study on the subject has shown that pure liquids, solids and many solutions exhibit the broad *'polymeric band'* at ~ 3600-3200 cm^{-1}.

Table 5 : Alkene and aromatic C—H bonds

	Group	**Bond, cm^{-1}**	**Remarks**
(i)	$—C \equiv C—H$	—3300 (s)	
(ii)		3095–3070 (m)	C—H stretching
(iii)		3040–3010 (m)	
(iv)	Aryl —H	3040–3010 (w)	Often obscured
(v)		970–960 (s)	C—H out of plane deformation when double bond is conjugated with a C=O group, this band is shifted towards 990 cm^{-1}.
(vi)	$RCH=CH_2$	995–984 (s). and 940–900 (s)	
(vii)	$R_2C=CH_2$	895–885 (s)	
(viii)		840–790 (m)	
(ix)		730–675 (m)	

Problem 5. ***Give the differences between UV-visible and IR spectroscopy.***

	UV-Visible Spectroscopy	IR Spectroscopy
1.	The region of UV-visible spectroscopy extends from 10 to 800 nm	The region of IR spectroscopy extends from 800 to 20,000 nm.
2.	As UV-visible radiations possess more energy, they are strong and so can cause electronic excitations.	IR radiations are weak and so cannot produce electronic excitations. They cause bending and stretching vibrations of organic bonds.
3.	Unsaturated and especially conjugated groups only absorb in this region.	All organic bonds and groups absorb in this region.
4.	UV absorption spectrum exhibits broad absorption bands.	IR spectrum exhibits sharp peaks.
5.	This spectroscopy gives an idea about the presence of carbonyl group and a conjugated system.	This spectroscopy gives an idea about the nature of the functional group in the molecule. It helps in identifying the complete structure of the compound.
6.	The spectra are usually expressed in terms of wavelengths in nm units.	The spectra are usually expressed in terms of frequencies in wave number (ν) units.

Problem 6. ***What type of potential energy curve is obtained for a simple harmonic oscillator?***

A simple harmonic oscillator is the one in which the restoring force (F) is proportional to the displacement (x) in accordance with Hooke's law, *i.e.*,

$$F = -kx$$

For a diatomic molecule, $x = R - R_e$, where R is distance to which the atoms have been stretched and R_e is the equilibrium distance between the two atoms. k is called the force constant.

For such an oscillator, the potential energy (V) is given by

$$V = \frac{1}{2}kx^2$$

This is the equation of a parabola. Therefore, a *parabolic potential energy* curve is obtained as shown in figure (10).

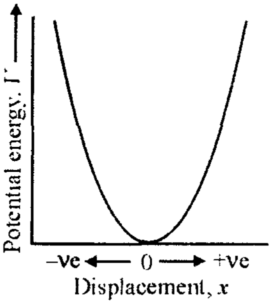


Fig. 10. Parabolic potential energy curve of a harmonic oscillator.

Problem 7. ***Mention an expression for vibrational energy of a diatomic molecule taking it as a simple harmonic oscillator. Sketch the vibrational energy levels of such a molecule.***

Using the concepts of quantum mechanics, it can be seen that if the vibratory motion of the nuclei of diatomic molecule (Fig. 11) is taken as equivalent to that of a **simple harmonic oscillator,** then the vibrational energy is obtained using quantum mechanics in the form of equation (1).

Fig. 11. Vibratory motion of a diatomic molecule.

$$E_v = \left(v + \frac{1}{2}\right)h\nu \qquad \ldots (1)$$

where, ν is the frequency of vibration and v is the vibrational quantum number with allowed values of 0, 1, 2, 3, etc.

Putting $\nu = \frac{c}{\lambda} = c\bar{\nu}_e$ or $c\omega_e$ where $\bar{\nu}_e$ or ω_e represents the equilibrium vibrational frequency in terms of wave numbers, equation (1) can be written as

$$E_v = \left(v + \frac{1}{2}\right)hc\omega_e \qquad \ldots (2)$$

Putting $v = 0, 1, 2, 3$ etc, in equation (2) it may be seen that the vibrational energy levels of a harmonc oscillator are equally spaced. These are shown diagrammatically in figure (12).

For the lowest vibrational level, $v = 0$. Therefore, the energy for the level will be

$$E_0 = \frac{1}{2}hc\omega_e \qquad \ldots (3)$$

This is called **zero point energy**. It means that even at *absolute zero when all translational and rotational motion cease in a crystal, the residual energy of vibration* E_0 *still remains, i.e., the vibrational motion still exists.*

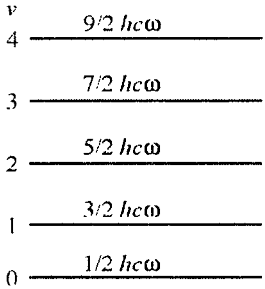


Fig. 12. Equally spaced vibrational energy levels of a harmonic oscillator.

Problem 8. ***Mention selection rules for vibrational transitions in a simple harmonic oscillator.***

The selection rule for a molecular vibration is that the *electric dipole moment must change when the atoms are displaced.* It should be noted here that the molecule need not have a permanent dipole. Based on this, the specific selection rule for vibrational transitions is $\Delta v = \pm 1$ *i.e.*, change in vibrational quantum number should be unity. Transitions for which $\Delta v = +1$ correspond to absorption and those with $\Delta v = -1$ correspond to emission.

Problem 9. ***What type of a vibrational spectrum is expected for simple harmonic oscillator in the form of a diatomic molecule ?***

Applying the selection rule, as the transitions can occur between vibrational levels whose vibrational quantum numbers differ by unity (*i.e.*, $\Delta \upsilon = \pm 1$), the energy absorbed by a diatomic molecule taking it as a simple harmonic oscillator, when the transition takes place from υ to $\upsilon + 1$ level will be given by

$$\Delta E_\upsilon = \left(v + 1 + \frac{1}{2} \right) hc\omega_e - \left(v + \frac{1}{2} \right) hc\omega_e = hc\omega_e$$

or $$\frac{\Delta E}{hc} = \omega_e$$

i.e., $$\Delta \bar{v} = \omega_e$$

Therefore, *only one absorption line* will be obtained in the vibrational spectrum whose wave number is equal to the equilibrium vibrational frequency of the diatomic molecule. Otherwise also, as the vibrational levels are equally spaced (Fig. 12), any transition from any v to $v + 1$ will give rise to the same energy change and, therefore, only one absorption line is expected. Further, at room temperature, as most of the molecules are in the lowest (ground state) vibrational level with $v = 0$, therefore, the transitions take place from $v = 0$ to $v = 1$. The frequency thus observed is called the **fundamental frequency.** These spectra are observed in the infrared (IR) region.

Problem 10. ***What types of molecules give vibrational spectra?***

The gross selection rule for a diatomic molecule to give a vibrational spectrum is that the *dipole moment of the molecule must vary when the atoms are displaced due to vibration.* The condition required is only the change in dipole moment and the molecule need not have a permanent dipole moment. For example, in case of homonuclear diatomic molecules like H_2, O_2, N_2 etc., which have only stretching motion/vibrations and no bending motion/vibrations, the dipole moment does not change during vibration. Therefore, these molecules do not give vibrational spectra, *i.e.*, they are said to be **infrared-inactive**. On the other hand, heteronuclear diatomic molecules like HCl, CO, NO etc., and polyatomic molecules like CO_2, H_2O, CH_4. C_2H_4 etc., which show change in dipole moment in some mode of vibration give vibrational spectra and are said to be ***infrared-active.***

NUMERICAL PROBLEM

Ex. 1. *Calculate the force constant for the bond in HCl from the fact that the fundamental vibration frequency is* 8.667×10^{13} s^{-1}.

Sol. m_1 (for H-atom) $= \dfrac{1.008}{6.022 \times 10^{23}}$ g $= 1.6739 \times 10^{-7}$ kg

m_2 (for Cl-atom) $= \dfrac{35.5}{6.022 \times 10^{23}}$ g $= 5.8951 \times 10^{-26}$ kg

$\therefore$ Reduced mass $\mu = \dfrac{m_1 \times m_2}{m_1 + m_2} = .6277 \times 10^{-27}$ kg

Also it is given that

$\omega = 8.667 \times 10^{13}\ s^{-1}$ $\therefore$ $k = 4\pi^2 \omega^2 \mu$

$= 4 \times (3.14)^2 \times (8.667 \times 10^{13})^2 \times (1.6277 \times 10^{-27}\ \text{kg})$

$=$ **483.1 Nm^{-1}.**

Problem 11. *What is Raman spectra or Raman spectroscopy? How will you explain Rayleigh's line, Stokes lines and anti-Stokes lines in Raman spectra?* (Meerut 2007)

Prof. C.V. Raman of Calcutta University, observed in 1928 that when a substance (gaseous, liquid or solid) is irradiated with monochromatic light of a definite frequency ν, the light scattered at right angles to the incident light contained lines not only of the incident frequency, but also of lower frequency and sometimes of higher frequency as well. This effect is known as **Raman effect.** The Raman scattering had been predicted by the German physicist A. Smekal (1923). It was observed by C.V. Raman and K.S. Krishnan (1920). The lines with *lower frequency* are called **Stokes lines**, whereas lines with *higher frequency* are called **anti-Stokes lines.** Line with the same frequency as the incident light is called **Rayleigh line**. Raman further observed that the difference between the frequency of the incident light and that of a particular scattered line was constant depending only upon the nature of the substance being irradiated and was completely independent of the frequency of the incident light. If ν_i is the frequency of the incident light and ν_s, that of a particular scattered line, the difference, $\Delta\nu = \nu_i - \nu_s$ is called **Raman frequency** or **Raman shift.** Thus, the Raman frequencies observed for a particular substance are characteristic of that substance. The spectrum so observed is called **Raman spectrum** as shown in figure (13).

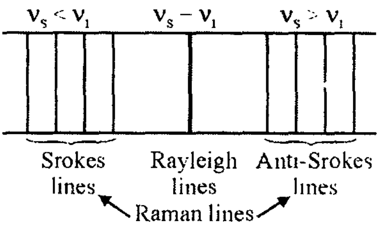


Fig. 13. A simplified repesentation of Raman spectrum.

[I] Rayleigh Line

When the photon strikes the molecule, the energy is absorbed by the molecule and it gets excited to some higher energy level. In case it returns to the original level, it will emit the same energy as absorbed and thus we have scattering known as *Rayleigh scattering* and the line is known as Rayleigh line.

[II] Stokes Lines

However, in most of the cases, the excited molecule does not return to the original level. It may return to a level higher than the original level, thereby emitting less energy than absorbed. This explains the occurrence of *Stokes lines*. Thus, a part of the energy of the incident photon remains absorbed by the molecule (so that molecule has higher energy than before).

[III] Anti-Stokes Lines

The excited molecule may return to a level lower than the original level. Thus, more energy is emitted than absorbed. This explains the occurrence of *anti-Stokes lines*. In this case, the molecule has less energy than before.

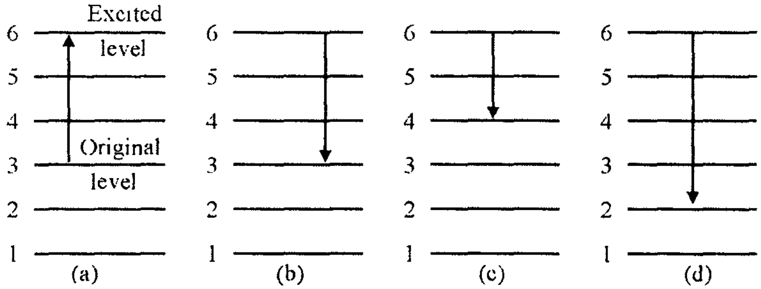


Fig. 14. (a) Energy absorbed by the molecule. (b) Rayleigh scattering. (c) Formation of Stokes lines (d) Formation of anti-Stokes lines.

The above different cases can be represented diagrammatically by figure (14).

Problem 12. ***Explain with mathematical equations the type of pure rotational Raman spectrum expected for a diatomic molecule.***

The selection rules for pure rotational spectrum of diatomic molecule are

$$\Delta J = 0, \pm 2$$

The selection rule $\Delta J = 0$ corresponds to Rayleigh scattering, whereas selection rule $\Delta J = \pm 2$ gives rise to Raman lines as explained below :

Energy of a rotational level (in terms of wave number) with quantum number J is given by,

$$\bar{\nu} = BJ\,(J + 1) \qquad \dots (1)$$

When a transition ocurs from a lower rotational level with quantum number J to a higher rotational level with quantum number J', the energy absorbed (in terms of wave numbers) will be given by,

$$\Delta\bar{\nu} = BJ'\,(J' + 1) - BJ\,(J + 1) \qquad \dots (2)$$

For the selection rule,

$\Delta J = +\,2$, *i.e.*, $J' - J = 2$, we get

$$\Delta\bar{\nu} = B\,(J + 2)\,(J + 3) - BJ\,(J + 1)$$
$$= B\,(4J + 6), \text{ where } J = 0, 1, 2, 3 \qquad \dots (3)$$

Now, for the selection rule,

$\Delta J = -\,2$, *i.e.*, $J' - J = -\,2$, we get

$$\Delta\bar{\nu} = BJ'\,(J' + 1) - B\,(J' + 2)\,(J' + 3)$$
$$= -\,B\,(4J' + 6), \text{ where } J' = 0, 1, 2, 3\dots \qquad \dots (4)$$

Combining the results of equations (3) and (4), the wave numbers of the lines obtained in the Raman spectrum will be given by

$$\bar{\nu} = \bar{\nu}_i \pm \Delta\bar{\nu}$$

or
$$\bar{\nu} = \bar{\nu}_i \pm B\,(4J + 6) \qquad \dots (5)$$

where $J = 0, 1, 2, 3, \dots$

Here $\bar{\nu}_i$ represents the wave number of the Rayleigh line, positive sign gives lines with higher wave numbers and are called anti-Stokes lines. The negative sign gives lines with lower wave numbers and are called Stokes lines.

From equation (5), it may be seen that for $J = 0$, $\bar{\nu} = \bar{\nu}_i = 6B$, *i.e.*, the first Stokes and anti-Stokes line will be at a separation of

$6B$ from the Rayleigh line. Further putting $J = 1, 2, 3, \ldots$ the separation between any two adjacent Stokes lines or anti-Stokes lines will be $4B$. Therefore, the pure rotational Raman spectrum expected for a diatomic molecule may be represented by figure (15).

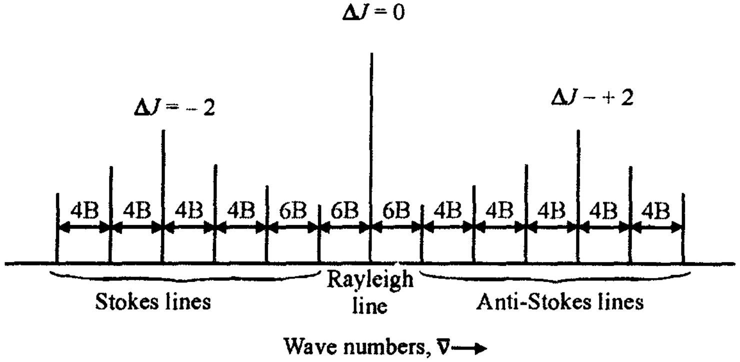


Fig. 15. Pure rotational Raman spectrum expected for a diatomic molecule.

Problem 13. ***What are the selection rules for rotational-vibrational Raman spectra of diatomic molecules? Describe rotational-vibrational Raman spectrum obtained for a diatomic molecule.***

Diatomic gaseous molecules give rotational-vibrational Raman spectra which are governed by the following selection rules :

$$\Delta v = \pm 1$$

$$\Delta J = 0, \pm 2$$

However, at room temperature, as most of the molecules are in the lowest vibrational level ($v = 0$), therefore, the significant vibrational transition is from $v = 0$ to $v = 1$ (called fundamental vibration transition). Restricting to this vibrational transition only, the following results are obtained :

For $\Delta J = 0$, $\Delta \bar{v} = \omega_e (1 - 2x_e)$ (called Q-branch).

For $\Delta J = +2$, $\Delta \bar{v} = \omega_e (1 - 2x_e) + B(4J + 6)$ (called S-branch).

For $\Delta J = -2$, $\Delta \bar{v} = \omega_e (1 - 2x_e) - B(4J' + 6)$ (called O-branch).

Expressing the values for Q, S and O branch by $\Delta\bar{v}_Q$, $\Delta\bar{v}_S$ and $\Delta\bar{v}_O$, respectively, and if the wave number of the exciting radiation be $\bar{v}_i$, the wave numbers of the Stokes lines will be given by,

$$\bar{v}_Q = \bar{v}_i - \Delta\bar{v}_Q$$

$$\bar{v}_S = \bar{v}_i - \Delta\bar{v}_S$$

$$\bar{v}_O = \bar{v}_i - \Delta\bar{v}_O$$

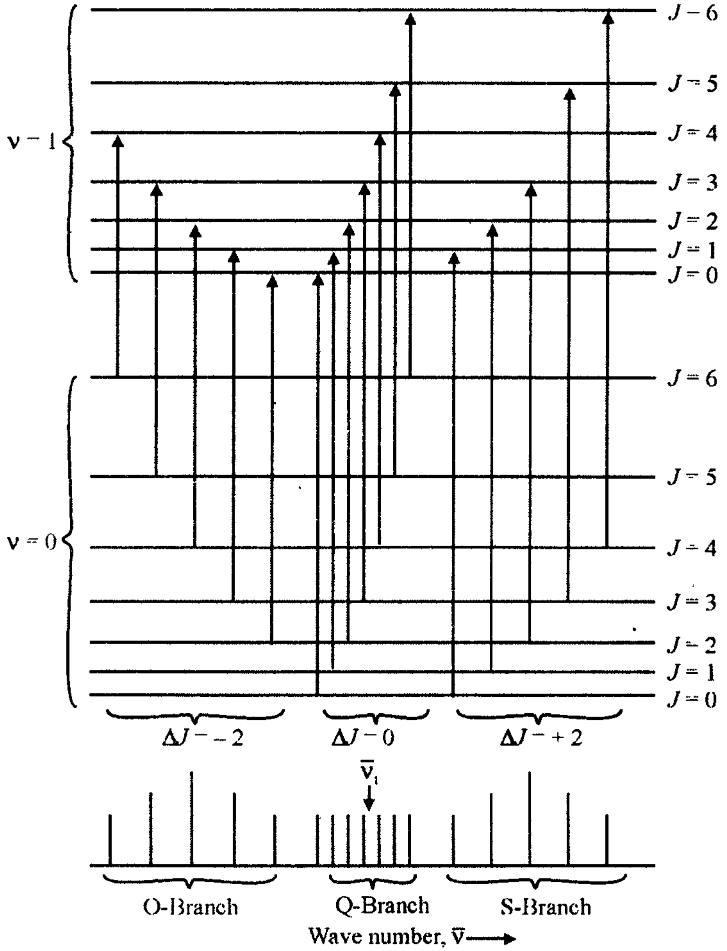


Fig. 16. Rotational-vibrational Raman spectrum of a diatomic molecule.

We have considered the case for $\Delta v = +1$ which represents Stokes lines. The anti-Stokes lines are those for which $\Delta v = -1$. They are usually weak because initially very few molecules are in the excited vibrational state.

The rotational transitions accompanying the vibrational transition from $v = 0$ to $v = 1$ and the rotational-vibrational Raman spectrum obtained may be represented by figure (16).

Problem 14. ***Explain Raman spectroscopy. Give an experimental set up of Raman spectrophotometer. Discuss some applications of Raman spectra.*** **(Meerut 2007, 2006)**

[I] Raman Spectroscopy

See Problem 11.

[II] Experimental Raman Spectroscopy

The experimental set up for Raman scattering is shown in figure (17). Intense monochromatic radiations from a source consisting of a large spiral discharge tube with mercury electrodes is allowed to fall on the cell containing a gaseous or liquid sample. When the current discharge passes through the tube, mercury emits lines in its spectrum the most intense of which at 4358Å (*i.e.*, 435.8 nm) serves as the exciting line. The scattered light is observed at right angles to the direction of the incident radiation. The detector is either a photographic plate or a photomultiplier. The horn shape of the cell helps in reducing the direct reflection of the source from the back of the cell.

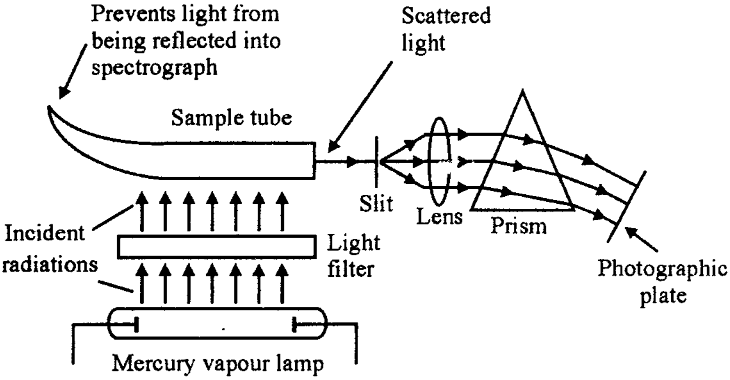


Fig. 17. The experimental set up for Raman spectroscopy.

The Raman spectra of gases are generally weaker than those of liquids. It is necessary to use very long discharge lamps and cells, the latter containing mirrors at both ends arranged so as to increase the effective path length of the cell. However, with the development of lasers, which are very powerful sources of monochromatic radiation, Raman spectroscopy has undergone radical changes.

[III] Applications of Raman Spectra

Raman spectroscopy, despite difficulties with sensitivity, has *several advantages* which make it an extremely important spectroscopic tool. It gives information about molecular vibrations that are inactive in the infrared region because of molecular symmetry. According to the ***'mutual exclusion rule'***, for centrosymmetric molecules (*i.e.*, molecules such as H_2, CO_2, C_2H_2, etc., that possess a centre of symmetry), the vibration which is active in infrared is inactive in Raman and the vibration which is inactive in infrared is active in Raman spectra. Raman spectroscopy, in fact, complements infrared spectroscopy. Thus, the stretching vibrations of homonuclear diatomic molecules (such as H_2, O_2, H_2, etc.) which are inactive in infrared (since they are not accompanied by a change in dipole moment which is already zero) are observed in Raman spectra. Also, the symmetric stretching vibration of CO_2, that is inactive in infrared, is active in Raman spectra.

Another example is that of planar dichloroethylene, $C_2H_2Cl_2$, which consists of *cis*- and *trans*-configurations in equilibrium. Only the *trans*-configuration has a centre of symmetry. Thus, the coincident frequencies observed in infrared and Raman spectra of the sample can be assigned to the *cis*-configuration. In this manner, the analysis of the mixtre of the *cis*- and *trans*-isomers can be carried out.

Again, for CS_2 all the vibrations that are Raman-active are infrared-inactive and vice-versa, whereas for N_2O the vibrations are simultaneously Raman and infrared-active. From the spectral data we conclude that CS_2 has a centre of symmetry, whereas N_2O has no centre of symmetry. Thus, the CS_2 structure is of the type S—C—S, while the N_2O structure must be N—N—O rather than N—O—N.

Raman spectroscopy has another advantage in that it uses visible or ultraviolet radiation rather than infrared radiation. Hence, the walls of the sample cell and other units of the optical system can be made of glass or quartz rather than of special materials that are transparent to infrared radiations. Also, the experimentalist can work very conveniently with aqueous media since water is far more transparent in the visible and UV regions than in the infrared region. Thus, Raman spectroscopy can be utilized for the investigation of biological systems such as the polypeptides and the proteins in aqueous solution.

Problem 15. ***What are the advantages of Raman spectroscopy over infrared spectroscopy ?***

Raman spectroscopy has a number of advantages over infra-red spectroscopy which are discussed below :

(1) Raman spectra can be obtained not only for gases but even for liquids and solids, whereas infrared spectra for liquids and solids are quite diffused.

(2) Since Raman frequencies are independent of the frequency of the incident radiation, so by suitably adjusting the frequency of the incident radiation, Raman spectra can be obtained in the visible spectrum range where they can be easily observed rather than the more difficult infrared range.

(3) Raman spectra can be obtained even for molecules such as O_2, N_2, Cl_2 etc., which have no permanent dipole moment. Such a study is not possible by infrared spectroscopy.

Problem 16. ***Write a note on P–Q–R bands in vibrational-rotational spectra.*** **(Meerut 2006)**

The vibrational-rotational spectrum of a substance does not occur in the form of a single spectral line. However, a number of lines appear on either side of the expected position. Consider the equation,

$$\bar{\nu} = \omega \pm \frac{h}{4\pi^2 I_c} \,.\, J \text{ (where } I_c = \text{moment of inertia)}$$

The first term on the right hand side, *i.e.*, ω (fundamental frequency of the vibration) gives the origin of centre of the fundamental band due to one step change in vibrational transition. The second term, *i.e.*, $\pm \frac{h}{4\pi^2 I_c}$ gives the rotational fine structure becasue of rotational transition.

(i) If ***J* is positive** then a series of lines of higher frequency (shorter wavelengths) appear on the right side of the band origin. These lines are known as ***R*–branch** of the vibrational-rotational band.

(ii) If ***J* is negative,** then a series of lines of lower frequencies (longer wavelengths) appear on the left side of the band origin. These lines are known as ***P*-branch** of vibrational-rotational band.

So, two lines appear, one on the right side and other on the left side of the origin for each possible value of *J*.

(iii) *J* may be close to zero, if the molecule has an angular momentum about the axis joining the nuclei. In such a case, vibrational transition is not accompanied by any appreciable rotational changes. The moment of inertia in the final state must, however, be different from that in the initial state. This shows that there must be some small changes in rotational energy of these molecules. These changes give rise to a series of very closely spaced lines, known as ***Q*-branch** or ***Q*-band.** Such bands are generally observed in polyatomic moelcules.

Problem 17. ***What types of molecules give rotational-vibrational Raman spectra?***

The selection rule for a molecule to give rotational-vibrational Raman spectrum is that the *polarization of the molecule must change as the molecule vibrates.* In case of both types of diatomic molecules, *i.e.*, homonuclear as well as heteronuclear, as the molecule vibrates, the control of the nuclei over the electrons changes and so there is a change in polarizability. That is why both types of diatomic molecules give rotational-vibrational Raman spectra, *i.e.*, they are *vibrational Raman-active.* This is one of the main advantages of Raman spectra over infrared spectra because homonuclear diatomic molecules do not give pure vibrational or rotational spectra because they do not possess a permanent dipole moment.

Problem 18. ***Write a short note on Franck-Condon principle.***

The nuclei in a molecule are subjected to different forces after an electronic transition has occurred and the molecule may respond by starting to vibrate. The resulting vibrational structure of electronic transitions can be resolved for gaseous samples, but in a liquid or solid, the lines usually merge together and result in a broad almost featureless band.

The vibrational structure of an electronic transition is explained by a principle known as Franck-Condon principle. According to it, **because the nuclei are so much more massive than the electrons, an electronic transition takes place very much faster than the nuclei can respond.**

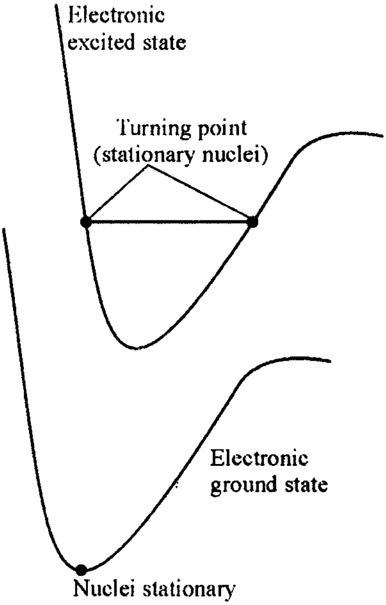


Fig. 18. According to the Franck-Condon principle, the most intense vibronic transition is from the ground vibrational state to the vibrational state lying vertically above it. Transitions to other vibrational levels also occur, but with lower intensity.

As a result of the transition, the electron density is rapidly built up in new regions of the molecule and removed from others and the initially stationary nuclei suddenly experience a new force field. They respond to the now force by beginning to vibrate and giving backwards and forwards from their original separation, which was maintained during the rapid electronic excitation. The stationary equilibrium separation of the nuclei in the initial electronic state, therefore, becomes a stationary turning point in the final electronic state (fig. 18).

Problem 19. ***Describe the concept of potential energy curves for bonding and antibonding molecular orbitals. What are the energy levels of molecular orbitals? Describe σ and π molecular orbitals.***

According to valency bond theory, a bond is formed by the overlapping of atomic orbitals and the bonded atoms in the molecule are held together by one or more pair of electrons. Thus, the electrons involved in the bond formation lose their identity but the atoms to some extent retain their identity even after the bond formation.

The molecular orbital theory given by Hund and Mulliken, considers that the valency electrons are associated with all the concerned nuclei, *i.e.*, with the molecule as a whole. Thus, in other words, the atomic orbitals combine together to form molecular orbitals in which the identity of both the atomic orbitals is lost. The number of resulting molecular orbitals is equal to the number of atomic orbitals involved in their formation. Thus, the combination of two atomic orbitals gives rise to two molecular orbitals. Of these, one molecular orbital is lower in energy, whereas other is higher in energy than the combining atomic orbitals.

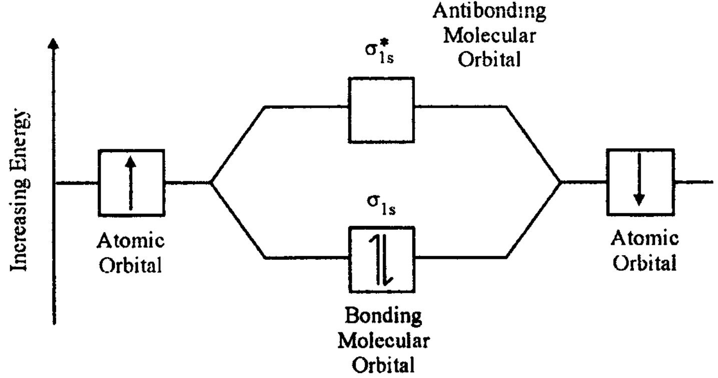


Fig. 19. Formation of bonding and anti-bonding molecular orbitals.

The molecular orbital having lower energy than combining atomic orbitals gives rise to an attractive state and is called as *bonding molecular orbital.* In such a molecular orbital, there will be a high probability of electron density in the overlapped region which will be in between the two positive nuclei. This high electron density in between the two positive nuclei shields them from mutual repulsion and keeps them together at the observed distance from each other as shown in fig. (20).

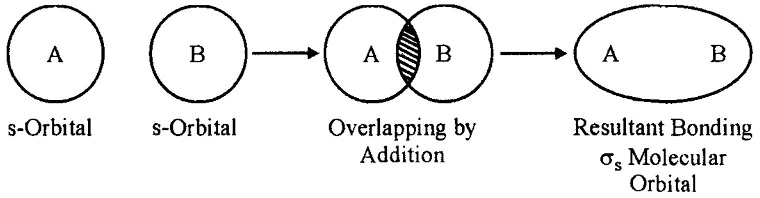


Fig. 20. Formation of bonding molecular orbital formed by the overlapping of *s*-orbital of one atom with *s*-orbital of another atom.

The molecular orbital having higher energy than the combining atomic orbitals gives rise to a repulsive state and is called as antibonding molecular orbital. In this case, the possibility of finding electrons in the region of overlap is practically nil. Thus, the electrons will not shield the two nuclei and on account of mutual repulsion, the nuclei will be pushed apart from each other as shown in figure (21).

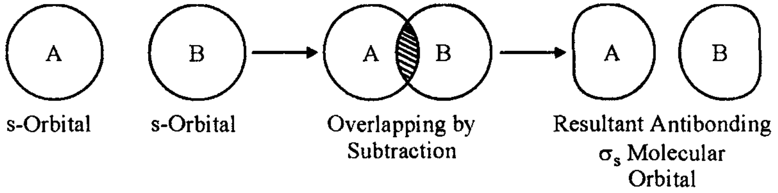

A
B
A
B
A
B
s-Orbital
s-Orbital
Overlapping by Subtraction
Resultant Antibonding σ_s Molecular Orbital

Fig. 21. Formation of antibonding molecular orbital formed by the overlapping of *s*-orbital of one atom with *s*-orbital of another atom. The +ve and – ve signs indicate the symmetry symbols.

[I] Conditions For the Combination of Atomic Orbitals

(1) The energies of the combining atomic orbitals should not differ much from one another.

(2) The atomic orbitals combine only if they overlap to a considerable extent. This will minimise the mutual repulsion between the nuclei.

(3) The combining atomic orbitals must have the same symmetry about the molecular axis.

The following types of molecular orbitals will be formed by the combination of *s* and *p* atomic orbitals.

First atomic orbital	Second atomic orbital	Type of molecular orbital formed
s	s or p_x or p_y or p_z	σ
p_x	s or p_x	σ
p_y	p_y	π
p_z	p_z	π

[II] Combination of Atomic Orbitals

(i) Combination of *s*-orbitals : The combination of two similar 1*s* atomic orbitals gives rise to two molecular orbitals, σ_{1s} and σ^*_{1s}. σ_{1s} is the bonding molecular orbital, where as σ^*_{1s} is the antibonding molecular orbital. Similarly, the combination of two 2*s* atomic orbitals will give rise to σ_{2s} and σ^*_{2s} molecular orbitals. These will be of higher energy than σ_{1s} and σ^*_{1s} molecular orbitals, as they are formed from atomic orbitals of higher energy.

(ii) Combination of *p*-orbitals : The *p*-orbitals can combine either along the axis to give σ-molecular orbitals or perpendicular to the axis to give π-molecular orbitals.

(a) Combination of p_x orbitals : The overlapping of two p_x orbitals along the axis results in the formation of a bonding σ_{p_x} and antibonding $\sigma^*_{p_x}$ molecular orbitals. The orbital with same sign produce bonding molecular orbitals, whereas the orbitals with unlike signs produce antibonding molecular orbitals.

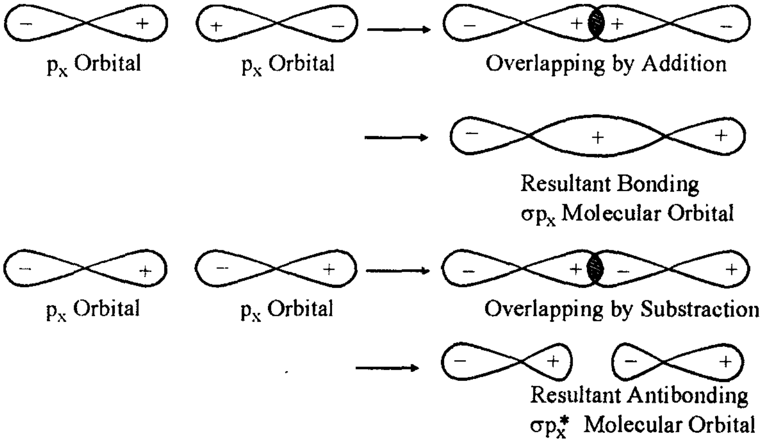


Fig. 22. Formation of bonding and antibonding σ molecular orbitals by the overlapping of p_x atomic orbitals.

(b) Combination of p_y or p_x orbitals : The overlapping of two p_y or two p_z atomic orbitals takes place perpendicular to the molecular axis and, thus, results in the formation of bonding and antibonding π-molecular orbitals shown in fig. (23).

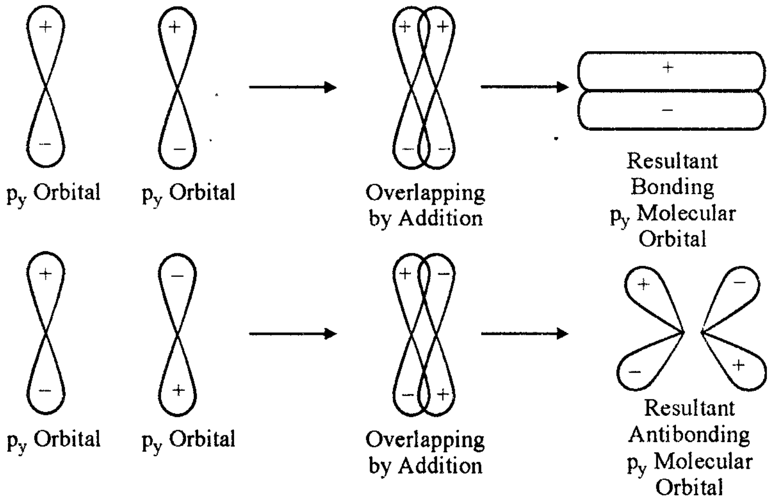


Fig. 23. Formation of bonding and antibonding π molecular orbitals by the overlapping of p_y or p_z atomic orbitals.

[III] Energy Levels of Molecular Orbitals

The mlecular orbitals involved in the formation of simple compounds are as follows :

Bonding molecular orbitals σ_{1s} σ_{2s} σ_{2p_s} π_{2p_y} π_{2p_z}

Antibonding molecular orbitals σ^*_{1s} σ^*_{2s} $\sigma^*_{2p_x}$ $\pi^*_{2p_y}$ $\pi^*_{2p_z}$

The energies of these molecular orbitals have been determined experimentally from spectroscopic data. The energy increases in the order as shown below :

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_x} < \pi_{2p_y} = \pi_{2p_z}$$
$$< \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

Thus, σ_{1s} possesses lowest and $\sigma^*_{2p_z}$ possesses the highest energy. This order is applicable for nitrogen and heavier homonuclear diatomic molecules. As the energies of σ_{2p_x} and π_{2p_y} or π_{2p_z} are very close together, the molecular orbitals for boron and carbon have slightly different pattern. In these cases, the energy of bonding σ_{2p_x} is higher than the nergy of bonding π_{2p_y} or π_{2p_z} orbitals.

[IV] Rules For the Filling of Electrons in the Molecular Orbitals

(1) The molecular orbitals are filled in the order of increasing energy.

(2) The maximum number of electrons in a molecular orbital is two.

(3) If there are two molecular orbitals of equal energy, they are first singly occupied and pairing starts when more electrons are to be filled.

Bond order or number of covalent bonds in the molecule

$$= \frac{1}{2} \text{ [Number of bonding electrons } - \text{Number of antibonding electrons]}$$

[V] Molecular Orbital Configuration of Some Molecules

(i) Hydrogen molecule : The electronic configuration of hydrogen is $1s^1$. When $1s$ atomic orbitals from two hydrogen atoms combine, there is a formation of σ_{1s} and σ^*_{1s} molecular orbitals. Since each hydrogen atom has only one electron, both the electrons will be present in the bonding σ_{1s} molecular orbital, the antibonding σ^*_{1s} will remain vacant. The molecular orbital configuration of H_2 molecule is, therefore, σ^2_{1s}.

The number of covalent bonds in the molecule

$$= \frac{1}{2} \text{ (Bonding electrons} - \text{Antibonding electrons)}$$

$$= \frac{1}{2}(2 - 0) = 1$$

Thus, there is a single covalent bond between two hydrogen atoms in the hydrogen molecule.

(ii) Nitrogen molecule : The atomic number of nitrogen is 7 and its electronic configuration is $1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$. When atomic orbitals of two nitrogen atoms combine, there will be 14 electrons to be filled in the molecular orbitals of N_2 molecule as follows :

$$[\sigma_{1s}^2\, \overset{*}{\sigma}_{1s}{}^2]\ [\sigma_{2s}^2\, \overset{*}{\sigma}_{2s}{}^2\, \sigma_{2p_x}^2\, \pi_{2p_y}^2\, \pi_{2p_z}^2]$$

or $$\mathrm{K\,K}\ [\sigma_{2s}^2\, \overset{*}{\sigma}_{2s}{}^2\, \sigma_{2p_x}^2\, \pi_{2p_y}^2\, \pi_{2p_z}^2]$$

where KK represents the closed K shell structure. The electrons of the closed shell do not take part in the bond formation and are known as non-bonding orbitals. Thus, there are 8 bonding and 2 antibonding electrons. The number of covalent bonds = (1/2) (8 – 2) = 3. This means that there is a triple covalent bond between two nitrogen atoms in a nitrogen molecule.

(iii) Oxygen molecule : The atomic number of oxygen is 8 and its electronic configuration is $1s^2\, 2s^2\, 2p_x^2\, 2p_y^1\, 2p_z^1$. When atomic orbitals of two oxygen atoms combine, there will be 16 electrons to be filled in the molecular orbitals of O_2 molecule as follows :

$$[\sigma_{1s}^2\, \overset{*}{\sigma}_{1s}{}^2]\ [\sigma_{2s}^2\, \overset{*}{\sigma}_{2s}{}^2\, \sigma_{2p_x}^2\, \pi_{2p_y}^2\, \pi_{2p_z}^2\, \overset{*}{\pi}_{2p_y}{}^2\, \overset{*}{\pi}_{2p_z}{}^1]$$

or $$\mathrm{K\,K}\ [\sigma_{2s}^2\, \overset{*}{\sigma}_{2s}{}^2\, \sigma_{2p_x}^2\, \pi_{2p_y}{}^2\, \pi_{2p_z}{}^2\, \overset{*}{\pi}_{2p_y}{}^1\, \overset{*}{\pi}_{2p_z}{}^1]$$

Thus, there are 8 bonding and 4 antibonding electrons. The number of covalent bonds = (1/2) (8 – 4) = 2. This means that there is a double covalent bond between two oxygen atoms in an oxygen molecule. The molecular orbital configuration also accounts for the paramagnetic character of O_2 molecule as there are two unpaired electrons in the antibonding π-orbitals.

(iv) Carbon monoxide molecule : The atomic number of carbon is 6 and that of oxygen is 8.

$${}_6\mathrm{C} = 1s^2\, 2s^2\, 2p_x^1\, 2p_y^1\, 2p_z^0\ ,$$

$${}_8\mathrm{O} = 1\mathrm{s}^2\, 2\mathrm{s}^2\, 2\mathrm{p}_\mathrm{x}^2\, 2\mathrm{p}_\mathrm{y}^1\, 2\mathrm{p}_\mathrm{z}^1$$

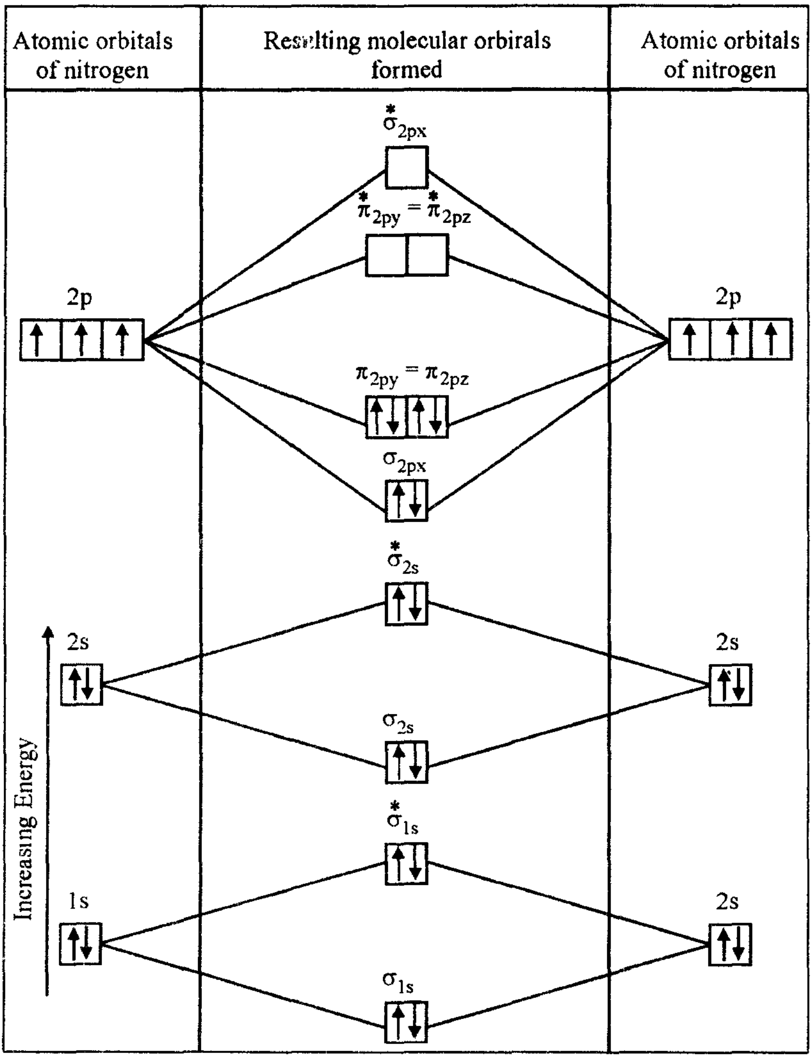
When atomic orbitals of carbon and oxygen combine, there will be 14 electrons to be filled in the molecular orbitals of CO molecule. The molecule of CO is isoelectronic with that of N_2. Hence, CO molecule will have the same molecular structure as that of N_2.

$$\mathrm{K\,K} \left\{ \sigma_{2s}^2\, \overset{*}{\sigma}_{2s}{}^2\, \sigma_{2p_x}{}^2\, \pi_{2p_y}{}^2\, \pi_{2p_z}{}^2 \right\}$$

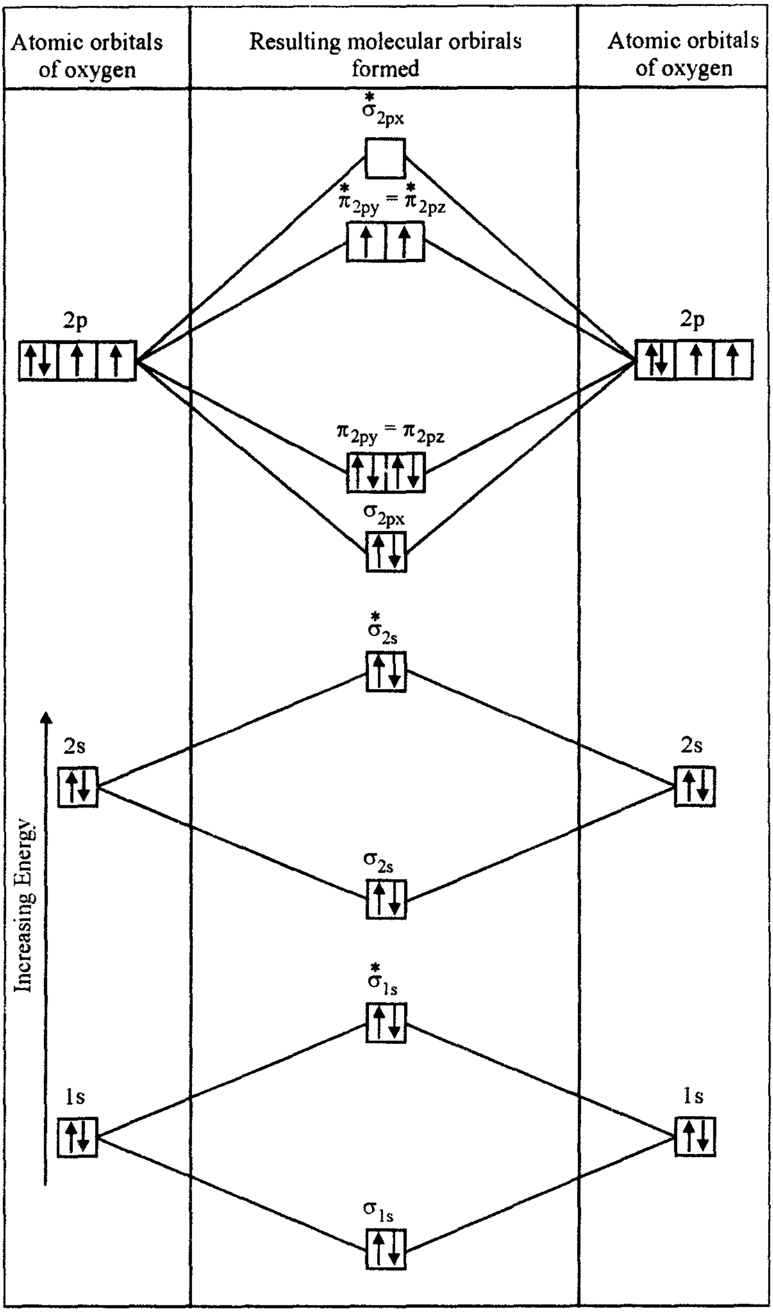
Thus, there are 8 bonding and 2 antibonding electrons. The number of covalent bonds = (1/2) (8 – 2) = 3. This means that there is triple bond between carbon and oxygen atoms.

Problem 20. ***Draw the molecular orbital energy level diagrams of N_2, O_2 and CO molecules.***

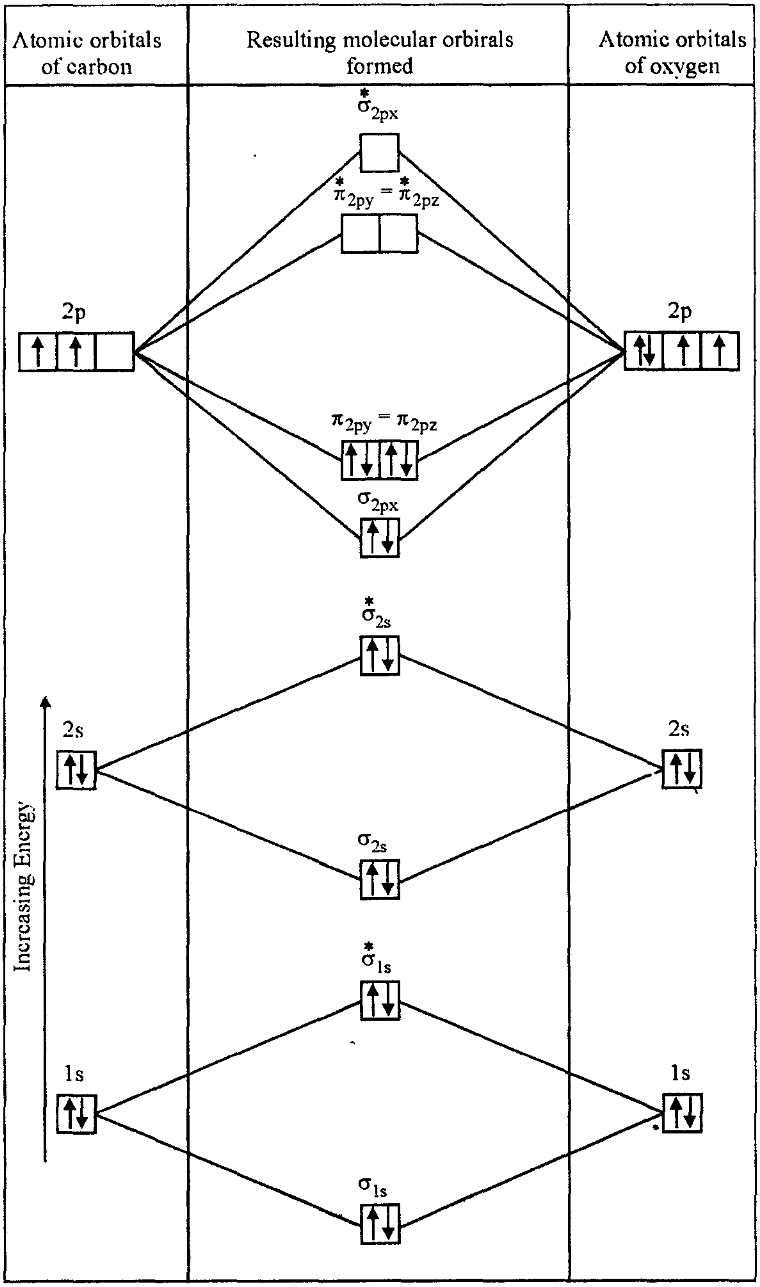
[I] Molecular Orbital Energy Level Diagram of N_2 Molecule


Atomic orbitals of nitrogen
Resulting molecular orbirals formed
Atomic orbitals of nitrogen
$\overset{*}{\sigma}_{2px}$
$\overset{*}{\pi}_{2py} = \overset{*}{\pi}_{2pz}$
2p
2p
$\pi_{2py} = \pi_{2pz}$
σ_{2px}
$\overset{*}{\sigma}_{2s}$
2s
2s
σ_{2s}
Increasing Energy
$\overset{*}{\sigma}_{1s}$
1s
2s
σ_{1s}

[II] Molecular Orbital Energy Level Diagram of O_2 Molecule


Atomic orbitals of oxygen
Resulting molecular orbirals formed
Atomic orbitals of oxygen
$\overset{*}{\sigma}_{2px}$
$\overset{*}{\pi}_{2py} = \overset{*}{\pi}_{2pz}$
2p
2p
$\pi_{2py} = \pi_{2pz}$
σ_{2px}
$\overset{*}{\sigma}_{2s}$
2s
2s
σ_{2s}
$\overset{*}{\sigma}_{1s}$
1s
1s
σ_{1s}
Increasing Energy

[III] Molecular Orbital energy Level Diagram of CO Molecule


Atomic orbitals of carbon
Resulting molecular orbirals formed
Atomic orbitals of oxygen
$\overset{*}{\sigma}_{2px}$
$\overset{*}{\pi}_{2py} = \overset{*}{\pi}_{2pz}$
2p
2p
$\pi_{2py} = \pi_{2pz}$
σ_{2px}
$\overset{*}{\sigma}_{2s}$
2s
2s
Increasing Energy
σ_{2s}
$\overset{*}{\sigma}_{1s}$
1s
1s
σ_{1s}

Problem 21. ***Mention the differences between bonding molecular orbital and antibonding molecular orbital.***

S.No.	Bonding molecular orbital	Antibonding molecular orbital
1.	They are formed by the linear combination of atomic orbitals when their wave functions are added $\Psi = \Psi_A + \Psi_B$	They are formed by the linear combination of atomic orbitals when their wave functions are subtracted $\Psi = \Psi_A - \Psi_B$
2.	They have lower energy (more stable) than the combining atomic orbitals.	They have higher energy (less stable) than the combining atomic orbitals.
3.	The electron density between the two positively charged nuclei is increased.	The electron density between the two positively charged nuclei is considerably decreased.
4.	The electrons of these molecular orbitals favour the stable bond formation	The electrons of these molecular orbitals oppose the bond formation.

EXERCISE

[I] Short Answer Type Questions

1. Explain Stokes lines, anti-Stokes lines and Rayleigh scattering in Raman spectrum.
   [For answer please see problem 11] **(Meerut 2007)**
2. What are units and ranges in infrared region ?
   [For answer please see problem 1]
3. Write important applications of infared spectroscopy.
   [For answer please see problem 4]
4. Give the potential energy curve for a simple harmonic oscillator.
   [For answer please see problem 6]
5. Mention the differences between UV-visible and infrared spectroscopy.
   [For answer please see problem 5]
6. Mention the selection rules for vibrational spectrum.
   [For answer please see problem 8]
7. Describe the selection rules for rotational-vibrational Raman spectrum.
   [For answer please see problem 13]
8. Write a note on P-Q-R branches of rotational-vibrational spectrum.
   [For answer please see problem 13] **(Meerut 2006)**
9. Mention the differences between Raman spectrum and infrared spectrum.
   [For answer please see problem 15]

10. Write a short note on Franck-Condon principle.
[For answer please see problem 18]
11. Mention the differences between bonding and antibonding molecular orbitals.
[For answer please see problem 21]
12. How will you determine force constant ?
[For answer please see problem 4]

[II] Very Short Answer Type Questions

1. Define Raman spectroscopy.
[For answer please see problem 11]
2. Define Rayleigh scattering.
[For answer please see problem 11]
3. Define Stokes and anti-Stokes lines.
[For answer please see problem 11]
4. What is Raman shift ?
[For answer please see problem 11]
5. Define Franck-Condon principle.
[For answer please see problem 18]
6. What do you understand by zero point energy ?
[For answer please see problem 8]
7. Define fundamental frequency.
[For answer please see problem 9]
8. Why H_2, O_2, N_2 molecules show vibrational spectrum ?
[For answer please see problem 10]
9. Explain why HCl, NO_2, C_2H_4 molecules show vibrational spectrum ?
[For answer please see problem 10]
10. Define the terms symmetric and antisymmetric stretching.
[For answer please see problem 2]
11. Arrange the energy required to produce rotational, vibrational and electronic transitions in increasing order. **(Meerut 2006)**
[**Ans.** Rotational < Vibrational < Electronic transitions]

❑❑❑

UNIT-3

PHOTOCHEMISTRY

Interaction of radiation with matter, difference between thermal and photochemical processes, Laws of photochemistry : Grotthus-Draper law, Stark-Einstein's law, Jablonski diagram depicting various processes occurring in the excited state, qualitative description of inter-system crossing, quantum yield, photosensitized reactions, energy transfer processes (simple examples).

PROBLEMS

Problem 1. ***What do you understand by photochemistry? What is the difference between thermochemical reactions and photochemical reactions?***

[I] Photochemistry

Photochemistry is that branch of science which deals with the chemical processes that occur when a material system is illuminated by radiation from an external source. So, **photochemistry** *is the science of chemical effects of radiations whose wavelengths lie in the visible and ultraviolet regions, i.e., in the range* from 8,000Å to 2,000 Å. The chemical effects produced by the high energy radiations like X-rays, γ-rays etc. are studied under ***radiation chemistry.***

[II] Thermochemical Reactions and Photochemical Reactions

Ordinary chemical reactions are referred to as **thermal** or **dark** reactions in order to distinguish them from the photochemical reactions. All spontaneous chemical reactions are accompanied by a decrease in the free energy, whereas photochemical reactions take place with an increase of free energy, as a result of free energy supplied by light.

[III] Differences between Photochemical Reactions and Thermochemical Reactions

	Photochemical reactions		**Thermochemical reactions**
1.	These reactions involve absorption of light.	1.	These reactions involve absorption or evolution of heat.
2.	The presence of light is the primary requisite for the reaction to take place.	2.	They can take place even in the dark.
3.	Temperature has very little effect on the rate of photochemical reaction. Instead, the intensity of light has a marked effect on the rate of a photochemical reaction.	3.	Temperature has significant effect on the rate of a thermochemical reaction.

4.	The free energy change (ΔG) of a photochemical reaction may not be negative. A few examples of photochemical reactions for which ΔG is positive and still they are spontaneous are synthesis of carbohydrates in plants and decomposition of HCl into H_2 and Cl_2.	4.	The free energy change (ΔG) of a thermochemical reaction is always negative.

Problem 2. ***Explain the different laws of photochemistry.***
(Meerut 2006)

Or, Write a short note on Stark-Einstein's law.
(Meerut 2007, 06)

[I] Laws of Photochemistry

(1) Grotthus-Draper law : According to this law, *'Only those rays which are absorbed by the substance are effective in producing a chemical change'.*

This statement was based on theoretical data. All light radiations which are absorbed are not, however, effective in bringing about chemical reactions. Some of the light radiations are converted into heat and some other re-emitted as radiations of the same or lower frequency.

(2) Lambert's law : According to this law, *'When a monochromatic beam of light passes through a homogeneous absorbing medium, equal fractions of incident radiations are absorbed by successive layers of equal thickness of the light absorbing substance'.* In other words, *'the rate of decrease of intensity with the thickness of absorbing medium is proportional to the intensity of the incident radiation'.*

Consider a thin layer of the medium of thickness dx and let I be the intensity of the radiation entering it, then mathematically, Lambert's law can be written as :

$$-\frac{dI}{dx} \approx I$$

or $$\frac{dI}{dx} = -kI. \qquad \text{(where } k = \text{constant)}$$

The value of I can be calculated by integrating the above equation within proper limits. *i.e.*,

or $$\int_{I_0}^{I} \frac{dI}{I} = -\int_0^x k dx$$

$$\log_e \frac{I}{I_0} = -kx$$

$$\frac{I}{I_0} = e^{-kx}$$

or $$I = I_0 \,.\, e^{-kx} \qquad \dots (1)$$

where, I_0 is the inensity of the incident radiation, and k is a constant which depends upon the nature of the medium as well as on the wavelength of light employed. The intensity of absorbed radiation,

$$I_{abs} = I_0 - I = I_0\,(I - e^{-kx}).$$

On converting natural logarithm to common logarithm, equation (1) may also be written as,

$$I = I_0 \,.\, 10^{-ax} \qquad \dots (2)$$

where $a = \frac{1}{2.303} k = 0.4343\, k$ and is known as extinction coefficient. It is this quantity which is called **absorption coefficient** or **absorptivity** of the substance. The factor $-\log (I/I_0)$ is called **absorbance** of the medium.

(3) Beer's law : Beer (1852) showed that the absorption of light by solution depends upon the thickness (x) of the layer traversed and the molecular concentration (c), in that layer. According to this law,

'The absorption of light remains constant when the concentration and the thickness of the absorbing layer are changed in an inverse ratio'. In other words, *'the rate of decrease in intensity of radiation absorbed is proportional to the intensity of the incident radiation and also to the concentration of the solution.'*

Mathematically, $$-\frac{dI}{dx} = \varepsilon c I$$

where c = concentration of the solution and ε is a constant.

On integration, $$\log_e \frac{I}{I_0} = -\varepsilon c x \qquad \dots (3)$$

or $$\frac{I}{I_0} = e^{-\varepsilon c x}$$

$$I = I_0\, e^{-\varepsilon c x}$$

This equation shows how the intensity of a monochromatic light falls from I_0 to I on passing through a thickness x of a solution of concentration, c.

It is evident that if the concentration is doubled and the thickness of the layer be halved, the extent of absorption will be the same. Rewriting equation (3), we get

$$2.303 \log_{10} \frac{I}{I_0} = -\varepsilon c x$$

$$\log_{10} \frac{I}{I_0} = -\frac{\varepsilon}{2.303} \cdot cx$$

or $$\log_{10} \frac{I}{I_0} = -\varepsilon' cx$$

or $$\frac{I}{I_0} = 10^{-\varepsilon' cx}$$

$$I = I_0 \cdot 10^{-\varepsilon' cx}$$

where ε' is known as *molar extinction coefficient* of the absorbing medium, and is given by $\varepsilon' = 0.4343\ \varepsilon$. Now, it is known as molar **absorption coefficient** or **molar absorptivity** of the absorbing solution. The value of ε' depends upon the nature of the substance and the wavelength of the incident light. The quantity, $\log_e (I_0/I)$ is called the **optical density or absorbancy** (D) of the medium, *i.e.*,

$$D = \log_e \frac{I_0}{I} = \varepsilon'.c.x. \text{ (where } x = \text{ thickness of medium).}$$

(4) Law of photochemical equivalence or Stark-Einstein's law : Stark (1909) and Einstein (1912) gave the most important law of photochemistry, based on quantum theory. According to this law,

'In a photochemical reaction, one quantum of active light (photon) is absorbed per molecule of the reacting substance which disappears'.

Suppose the frequency of the absorbed light be ν. Then the corresponding quantum of energy absorbed per molecule will be $h\nu$, where h is Planck's constant. Therefore, the quantum of energy, E absorbed per mole of the reacting substance is given by,

$$E = Nh\nu \text{ erg mole}^{-1} \text{ (where } N = \text{Avogadro's number)}$$

$$= \frac{Nh\nu}{4.184 \times 10^7} \text{ cal mole}^{-1}.$$

$$\therefore \quad E = \frac{(6.023 \times 10^{23}) \times (6.626 \times 10^{-27}) \times \nu}{4.184 \times 10^7} \text{ cal mole}^{-1} \qquad \ldots (4)$$

Now $\nu = c/\lambda$, where c is the velocty of light and λ is the wavelength of radiation absorbed.

$$\therefore \quad E = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-27} \times 2.998 \times 10^{10}}{4.184 \times 10^{7} \times \lambda}$$

$$= \frac{2.86}{\lambda} \text{ cal mole}^{-1}. \qquad \ldots (5)$$

In equation (5), λ is expressed in cm, but it is generally expressed in Angstrom unit, Å (1Å = 10^{-8} cm). Thus,

$$E = \frac{2.86}{\lambda} \times 10^{8} \text{ cal mole}^{-1} = \frac{2.86}{\lambda} \times 10^{5} \text{ kcal mole}^{-1}$$

$$= \frac{11.97 \times 10^{5}}{\lambda} \text{ kJ mole}^{-1}.$$

Thus, it is clear, that the numerical value of E varies inversely with the wavelength of the light absorbed. Therefore, shorter the wavelength, the greater is the energy absorbed per mole. The quantity E, *i.e.*, energy absorbed per mole of the reacting substance is called **one einstein**, *i.e.*,

$$1 \text{ einstein} = \frac{2.86 \times 10^{5}}{\lambda} \text{ kcal mole}^{-1} = \frac{11.97 \times 10^{5}}{\lambda} \text{ kJ mole}^{-1}.$$

For violet light, $\lambda = 3750$ Å and $E = 76.2$ k cals and for red light, $\lambda = 7500$ Å and $E = 38.13$ k cals.

Problem 3. ***What do you understand by quantum efficiency? Write its values for some photochemical reactions. Describe the method for determining the quantum efficiency of a photochemical reaction. Give reasons of low and high quantum efficiency.*** **(Meerut 2007, 06, 05)**

[I] Definition of Quantum Efficiency

Quantum efficiency is defined as, *'the number of moles of the light absorbing substance that react chemically for each einstein of absorbed radiation'*, or *'the number of molecules reacting for each quantum of absorbed radiation'*. It is represented by ϕ.

Mathematically,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quantum of light absorbed in the same time}}$$

$$= \frac{\text{Number of moles or gram molecules reacting in a given time}}{\text{Number of einsteins of light absorbed in the same time}}.$$

[II] Experimental Determination of Quantum Efficiency

The determination of quantam efficiency requires :

(a) The determination of the number of moles of the reacting substance that undergo chemical change in a given time.

(b) The number of einsteins of radiation absorbed by the light absorbing substance during that time.

The former factor can be determined by the usual analytical methods. However, the apparatus employed for determining the latter factor consists of the following units :

(i) Light source : Sunlight, arc light, mercury vapour lamp etc. are used for this purpose.

(ii) Monochromator : Since the value of einstein depends upon the wavelength of the incident light, it is necessary to use light of one wavelength of light falling within a narrow range of wavelengths. Usually, discharge tubes giving atomic spectra are used. The line of desired wavelength is chosen by the use of properly chosen optical filters, which absorb the undesired wavelengths. Such device of using light of one wavelength, *i.e*, monochromatic light or light falling within a narrow range of wavelengths, is called a **monochromator**.

(iii) Reaction cell : The light from the monochromator enters a reaction cell A which contains the reaction mixture. The cell is generally made of glass or quartz with optical plane windows for the free exit and entrance of light radiation.

(iv) Detector : A detector B is used for determining the intensity of light coming from a reaction cell. The intensity of light is measured with the cell when empty and then with the reaction mixture. The difference between the two readings will give the amount of energy absorbed by the reaction system under study.

The schematic diagram is represented as :

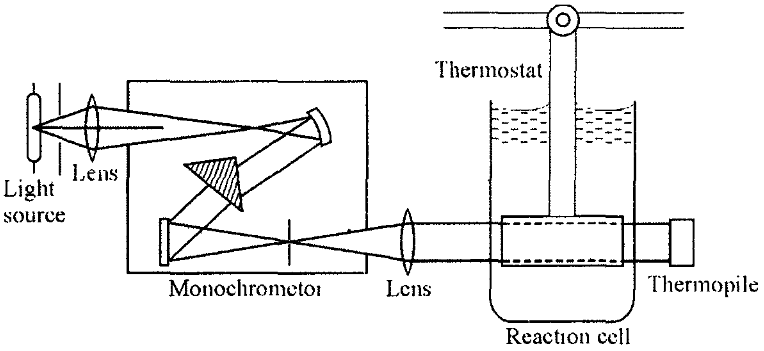


Fig. 1. An apparatus for photochemical experiments.

The intensity of light can be measured by the following type of detectors :

(a) Chemical actinometers : When extreme accuracy is not desired, a chemical actinometer can be used to measure the intensity of light radiation. It generally consists of gas mixtures or solutions which are sensitive to light. When radiations fall upon these substances, a chemical reaction takes place and the extent of it gives a direct measure of energy absorbed.

The most frequently used actinometer is the uranyl oxalate actinometer. It consists of a 0.05 M solution of oxalic acid mixed with an equal volume of 0.01 M of uranyl nitrate or sulphate. On exposure to violet or ultraviolet light within wavelengths of 2540 Å and 4350 Å, oxalic acid gets decomposed, the uranyl ion (UO_2^{2+}) acting as a photosensitizer. The extent of the decomposition during a given period of time is determined by titration with standard $KMnO_4$ at the beginning and at the end of the exposure. The difference in the readings gives a measure of intensity of light absorbed.

$$UO_2^{2+} + h\nu \rightarrow (UO_2^{2+})^*$$

$$(UO_2^{2+})^* + (COOH)_2 \rightarrow CO_2 + CO + H_2O + (UO_2^{2+}).$$

(b) Thermopile : It consists of a series of unlike metals which are connected to a galvanometer. One end of it is coated with lamp black or platinum black and the other end is kept as such. The thermopile is kept in glass or quartz vessel. When light from a reaction cell is incident on the black surface, it gets heated up, resulting in a difference in temperatures of the black and the other cold end. So, a thermo-electric current flows in the circuit. The current produced is proportional to the intensity of light absorbed. Thermopiles are generally calibrated with standard light sources.

[III] Method for the Determination of Quantum Efficiency

First set up the apparatus as shown in figure (1). Then an empty cell or the cell filled with solvent (only in case of solutions), is placed in the path of the light beam and the light intensity is determined as such. Now fill the reaction vessel with the reaction mixture. Allow the light to pass through it for a known time. Then note the intensity of light after the reaction is over. The difference between the two readings will give the total energy absorbed by the reacting mixture in the given time. If the time is 1 second, the total energy absorbed divided by the volume of the reaction mixture gives the intensity of the radiation absorbed. Analyse the contents of the reaction mixture. Then determine the number of moles reacted in a given time. The value of ϕ is calculated as follows :

$$\phi = \frac{\text{No. of moles reacting in a given time}}{\text{No. of einsteins absorbed in the same time}}$$

[IV] Quantum Efficiencies of Some Photochemical Reactions

Some photochemical reactions with quantum yield or efficiency are mentioned in the following table.

S. No.	Photochemical Reaction	Wavelength (Angstroms)	Quantum Yield
	Liquid Phase :		
1	$2Fe^{2+} + I_2 \rightarrow 2Fe^{3+} + 2I^-$	5,780	1
2.	$SO_2 + Cl_2 \rightarrow SO_2Cl_2$	4,200	1
3.	$H_2S \rightarrow H_2 + S$	2,080	1
	Gas Phase :		
1.	$2HI \rightarrow H_2 + I_2$	2,070–2,810	2
2.	$2HBr \rightarrow H_2 + Br_2$	2,070–2,540	2
3.	$H_2 + Cl_2 \rightarrow 2HCl$	2,000	10^5
4.	$CO_2 + Cl_2 \rightarrow 2COCl$	4,000–4,350	10^3
5.	$2NH_3 \rightarrow N_2 + 3H_2$	2,100	0.2
6.	$3O_2 \rightarrow 2O_3$	1,710–1,900	3
7.	$H_2 + Br_2 \rightarrow 2HBr$	5,100	0.1

[V] Reasons for High and Low Quantum Efficiencies

On the basis of values of quantum efficiencies, the different photochemical reactions can be divided into three categories :

(1) Those in which the quantum efficiency is a small integer, *e.g.*, 1, 2 or 3. Examples are combination of sulphur dioxide and chlorine and dissociation of hydrogen bromide, etc.

(2) Those in which the quantum efficiency is very high, *e.g.*, combination of hydrogen and chlorine etc.

(3) Those in which the quantum efficiency is very low, *e.g.*, combination of hydrogen and bromine etc.

In order to explain the above variations, Bodenstein pointed out that photochemical reactions involve two processes, *i.e.*,

(a) ***Primary process :*** In this process, the light quantum $h\nu$ is absorbed by a molecule A resulting in the formation of an excited molecule A^*. Thus,

$$A + h\nu \rightarrow A^*$$

The molecule which absorbs light may get dissociated giving atoms or free radicals.

(b) ***Secondary process :*** In this process, the excited atoms, molecules or free radicals produced in the primary process react further.

(1) Reasons for high quantum efficiency : The reasons for high quantum efficiencies are :

(i) Sometimes, the atoms or free radicals initiate a series of chain reactions, *e.g.*, in the combination of H_2 and Cl_2 to give HCl and the quantum efficiency is of the order of 10^6 or even more.

(ii) The secondary reaction is exothermic, so that the heat of reaction may activate other molecules thereby causing them to react.

(iii) The activated molecules may not get deactivated before forming the products.

(2) Reasons for low quantum efficiency : The reasons for low quantum efficiencies are :

(i) Excited molecules may get deactivated before they form the products.

(ii) The primary photochemical process may get reversed as in the combination of H_2 and Br_2 to form HBr and the quantum efficiency is of the order of 0.01.

(iii) Collisions of excited molecules with non-excited molecules may cause the former to lose their energy.

(iv) The dissociated fragments may recombine to form the original molecule.

Problem 4. ***What do you understand by excited states? Define and discuss the characteristics of singlet and triplet states.***

[I] Excited States

The absorption of photons of UV and visible radiations supplies an amount of energy which is sufficient to cause the electronic transitions in the molecules and the molecule is said to have promoted to the excited molecular electronic state from the lower or ground molecular electronic state. During this electronic transition, changes in the rotational and vibrational quantum numbers may also occur, giving rise to a band spectrum.

Electronic emission spectra of molecules originate in transitions from excited molecular electronic states. These excited states can be produced by electron impact, by heading to high temperature, or by the absorption of light. Emission spectra, more complex than absorption spectra, in the sense that more bands, including those corresponding to transitions to $V = 1, 2, 3, \ldots$ in the ground electronic state, can be observed. According to *Franck-Condon principle,* ***the most probable electronic transitions are those in which separation and kinetic energy of nuclei do not change.***

Absorption of energy by a molecule in the lower molecular electronic state with $V = 0$ produces an electronically excited molecule with the same inter-nuclear separation. The instantaneous final state, therefore, lies vertically above the initial state.

From the above facts it has become quite clear that *the excited state of a molecule is a state which results from a molecular electronic transition.*

[II] Singlet and Triplet States

Singlet and triplet states arise from multiplicity considerations of spectroscopy and simply define *the number of unpaired electrons in the absence of a magnetic field.* The systems having 0, 1, 2, 3, ... unpaired electrons refer to singlet, doublet, triplet, ..., respectively. If there are n number of unpaired electrons, it means that $(n + 1)$ fold degeneracy (equal energy states) will be associated with the electron spin, irrespective of the molecular orbitals occupied. *So, if no unpaired electrons are present, i.e., n = 0, then degeneracy will be one and such a state is called the* **singlet state.** In most of the organic molecules, all the electrons are paired (*i.e.*, electrons have anti-parallel spins, ↑↓) in their ground state. This is called **ground singlet state.** In such a state, the orbitals corresponding to ground energy level (ground electronic state) are occupied by electrons with paired-spins (anti-parallel spins, ↑↓), *i.e.*, no unpaired electrons, while the orbitals corresponding to higher energy levels are vacant.

When the molecule in the ground singlet state absorbs UV or visible radiations of proper frequency, one electron passes into the vacant orbitals present in higher energy level. During such transition two spin relationships may result.

(1) *The promoted electron can have a spin anti-parallel to its original partner*, which is called **excited singlet state.**

(2) *The promoted electron can have a spin parallel to its original partner*, which is called **excited triplet state.**

Therefore, the *ground singlet state* of the system has no unpaired electrons in the ground electronic state. The excited *singlet state* of the system has two electrons—one in ground state and the other in higher energy state but spins of both are anti-parallel and so no unpaired electron. However, in the *excited triplet state* of the system the two electrons (one in ground state and the other in the higher energy state (excited state)) have their spins parallel. These states are tabulated in figure (2).

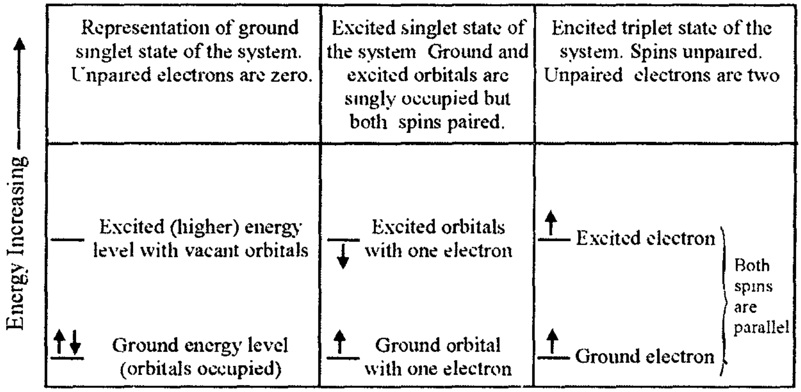

Energy Increasing
Representation of ground singlet state of the system. Unpaired electrons are zero.
Excited singlet state of the system Ground and excited orbitals are singly occupied but both spins paired.
Encited triplet state of the system. Spins unpaired. Unpaired electrons are two
Excited (higher) energy level with vacant orbitals
Ground energy level (orbitals occupied)
Excited orbitals with one electron
Ground orbital with one electron
Excited electron
Ground electron
Both spins are parallel

Fig. 2. Picture representation of ground singlet state, excited singlet state and excited triplet state of the system.

The above types of transitions are very common in π-systems, *i.e.*, $\pi \rightarrow \pi^*$ transitions, because π-electrons can be easily promoted than σ-electrons.

Theoretically, the electronic transitions are governed by a **spin conservation rule,** according to which the *transitions between states of different multiplicity are forbidden.* For example, transitions from singlet to triplet and vice-versa are forbidden, *i.e.*, such transitions have very small probability of occurrence in practice.

[III] Characteristics of Singlet and Triplet States

The singlet and triplet states possess the following properties:

(1) Life time : The life time of *excited singlet state* is 10^{-9} to 10^{-6} sec, while that of *excited triplet state is* 10^{-5} to 10^{-3} sec. Hence, lifetime of the former is much shorter.

(2) Energy : The excited triplet state is usually lower in energy than the excited singlet state in accordance with Hund's multiplicity rule. Therefore, singlet state is more reactive than the triplet state.

(3) Magnetism : The singlet state is diamagnetic as it has no unpaired electrons, while the excited triplet state is paramagnetic.

(4) The excited triplet state gives a 'biradical', since the two unpaired (parallel) electrons can be assumed to behave like two non-interacting electrons.

Problem 5. *Explain the following :*

(i) Non-radiative transitions, internal conversion and inter-system crossing.

(ii) Radiative transitions

(iii) Jablonski diagram expressing molecular energy levels in photochemical processes. **(Meerut 2005)**

[I] Non-Radiative Transitions

The excited molecules can lose their energy in the following two ways :

(1) By non-radiative transitions or

(2) By radiative transitions.

Non-radiative transitions : *The transition from excited singlet state (S_1) to ground singlet state (S_0), i.e., $S_1 \rightarrow S_0$, are called non-radiative transitions.* It is also called ***internal conversion (I.C.).*** It can also take place between triplet states in the same manner, *e.g.*, $T_2 \rightarrow T_1$, *i.e.*, from higher triplet state (T_2) to the lower triplet state (T_1).

In some molecules, there is a triplet state (T_1) close to an excited singlet state (S_1) and due to this the molecule can cross over into triplet state. Such type of transition, *i.e.*, $S_1 \rightarrow T_1$ is called ***inter-system crossing (ISC).*** It is also a non-radiative transition. The non-radiative transitions do not emit any radiations.

[II] Radiative Transitions

Radiative transitions are accompanied with emission of radiations and are of two type, viz., *fluorescence and phosphorescence.*

(1) Fluorescence : When the molecules are exposed to UV or visible light of a suitable frequency, it will be absorbed in a femto second (10^{-15} sec) and the molecule moves from the ground singlet state to the first excited singlet state. Since the average life time of this excited singlet state is very very small (10^{-9} – 10^{-6} sec), a direct transition from the excited singlet state back to the singlet ground state may occur with the emission of photons (radiations). This kind of emission of radiation is called **fluorescence.** The mechanism of fluorescence is as follows :

$$\underset{(S_0)}{\text{Molecule}} \xrightarrow[\text{Absorption}]{h\nu} S_1 \xrightarrow[\text{transition}]{\text{Radiative}} S_0 + h\nu'$$

(2) Phosphorescence : This phenomenon is another possibility of the radiative transition. After the absorption of light of a suitable wavelength, the molecule is raised to excited singlet state (life time 10^{-9} – 10^{-6} sec). It may undergo transition to a *metastable triplet* state (life time 10^{-5} – 10^{-3} sec) and some time thereafter returns back to the stable singlet ground state by emission of an ultraviolet or visible radiation photons. This kind of

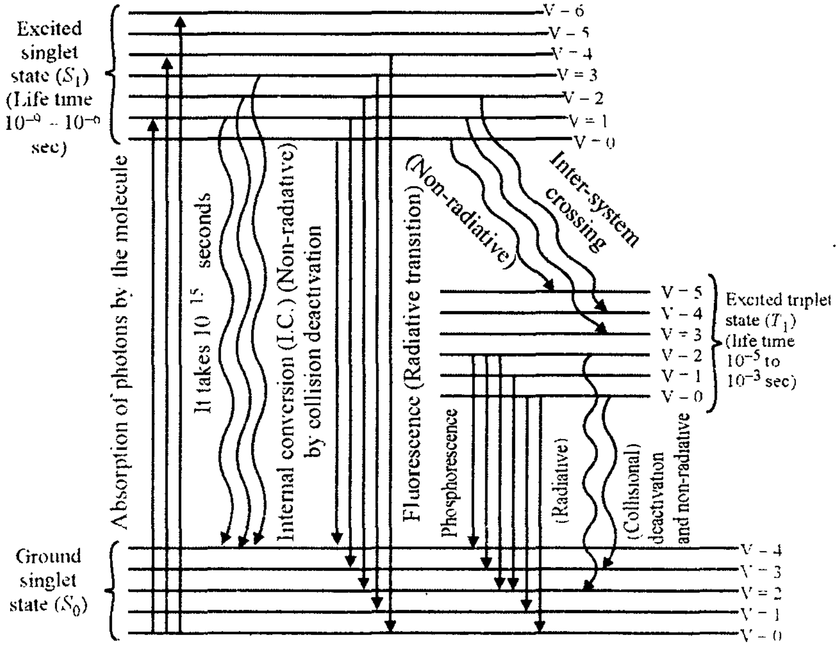

Excited singlet state (S_1) (Life time 10^{-9} - 10^{-6} sec)
V - 6
V - 5
V - 4
V = 3
V - 2
V = 1
V - 0
Absorption of photons by the molecule
It takes 10^{-15} seconds
Internal conversion (I.C.) (Non-radiative) by collision deactivation
Fluorescence (Radiative transition)
(Non-radiative)
Inter-system crossing
Phosphorescence
(Radiative)
(Collisional) deactivation and non-radiative
V - 5
V - 4
V = 3
V - 2
V - 1
V - 0
Excited triplet state (T_1) (life time 10^{-5} to 10^{-3} sec)
Ground singlet state (S_0)
V - 4
V - 3
V = 2
V - 1
V - 0

Fig. 3. Representation of molecular energy levels involved in photochemical processes by Jablonski diagram.

radiative transition is called ***phosphorescence.*** The process of crossing from excited singlet state to a metastable triplet state is called ***inter-system crossing*** and it does not involve any emission of photons, hence it is a non-radiative transition. The mechanism of phosphorescence is as follows :

$$\begin{array}{c}\text{Molecule}\\ \text{(Ground singlet)}\\ \text{state, }(S_0)\end{array} \xrightarrow[\text{Absorption}]{\text{h}\nu} S_1 \xrightarrow[\text{I.S.C.}]{\text{Non-radiative}} T_1 \xrightarrow[\text{transition}]{\text{Radiative}} S_0 + h\nu'$$

[III] Jablonski Diagram

The excited state processes in the molecules are pictorially represented in figure (3) known as Jablonski diagram.

Problem 6. *Write a note on photosensitization.* **(Meerut 2005)**

In order to bring about a photochemical reaction, it is necessary to have a certain minimum energy; the reactive system must be illuminated by light of corresponding wavelength, equal to or shorter than a certain maximum. *This maximum wavelength is called the **photochemical threshold.***

It is sometimes found that the substance used in the photochemical reaction may not absorb the light used. It is then necessary to introduce into the system a third substance capable of absorbing this wavelength. If this energy is sufficient to cause reaction and if the absorbing substance is not permanently transformed, then this phenomenon is known as **photosensitization.** Reactions brought about in this way are said to be **photosensitized** and the light absorbing but non-reacting substance is known as the **photosensitizer.** Since photosensitizer is not destroyed in the process, it is thus clear that only a very small amount may be effective. At first sight, photosensitization may be treated to be a kind of chemical catalysis.

Vogel (1873) discovered that photographic plates could be sensitized to green and red light, by treating them with certain dyestuffs. Atoms, such as those of mercury, xenon etc. are effective. Those reactions where halogen molecules are photosensitizers generally include decompositions and rearrangements. Chlorophyll sensitizes the photosynthesis of carbohydrates, zinc oxide sensitizes some photo-oxidations and reduction of organic compounds.

The explanation of photosensitization falls under two heads *viz.*, according to *whether the direct result of light absorption is the* *excitation of the photosensitizer to a higher electronic level or its dissociation.* In the former case, the reaction is induced by a transfer of energy of excitation to a molecule of the reactants so as to activate it for the chemical change. In the latter case, the products of dissociation catalyse the chemical change.

It has been seen that atoms can be excited to various levels by the absorption of light of an appropriate wavelength. The importance of such excited atoms in connection with photochemistry lies in their ability to initiate the secondary reactions in the process known as **photosensitization**. These secondary reactions had to compete with the spontaneous emission of the excited species. The question of radioactive life time is, therefore, of importance from the stand-point of its effectiveness as a photosensitizer. *Excited atoms with a long life time are most effective in initiating such reactions.* Thus, in the case of Hg atom as a sensitizer on exposure to 2537 A, it is first excited to $^3P_1$ state according to the equation

$$Hg(^1S_0) + h\nu \longrightarrow Hg^*(^3P_1)$$

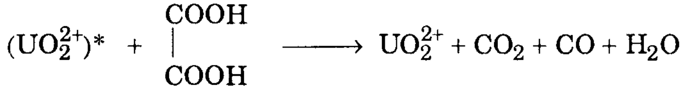
These excited mercury atoms in the $^3P_1$ state is readily converted to $^3P_0$ state. The radioactivity transition from Hg^* $(^3P_0)$ state to the unexcited ground level state of Hg $(^1S_0)$ is highly improbable from the selection rule. Therefore, the $Hg^*(^3P_0)$ *atoms have long lives and are, therefore, very effective in bringing about photosensitization.*

Examples of Photosensitization

A few well known examples of the photosensitized reactions are briefly described as under :

(1) Decomposition of oxalic acid in presence of uranyl sulphate : This reaction forms the basis of the actinometer used to measure the intensity of radiation. The coloured uranyl ions absorb light and gets activated $[(UO_2^{2+})^*]$. The activated ions then pass the light to the colourless oxalic acid which then undergoes decomposition; the extent of decomposition depending upon the light energy absorbed.

$$UO_2^{2+} + h\nu \longrightarrow (UO)^{*2+}_2$$



$$(UO_2^{2+})^* + \begin{array}{c}COOH\\|\\COOH\end{array} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The uranyl ions thus act as photosensitizer.

(2) Dissociation of hydrogen molecules in presence of mercury vapour : Hydrogen molecules do not dissociate when exposed to ultraviolet light. However, when hydrogen gas is mixed with mercury vapour and then exposed to the ultraviolet light, hydrogen molecules dissociate to give hydrogen atoms through the following reactions :

$$Hg + h\nu \longrightarrow Hg^*$$

$$Hg^* + H_2 \longrightarrow Hg + 2H$$

where Hg^* represents the activated mercury atom. Thus, in the above reaction mercury atom acts a photosensitizer.

The H-atom being highly reactive can easily reduce metallic oxides, nitrous oxide, carbon monoxide etc.

Problem 7. ***Write a detailed note on fluorescence.***

(Meerut 2007, 05)

When a substance mostly vapour or liquid is irradiated by light, it itself begins to emit light and it stops emitting light or radiation as soon as the incident light is cut off. This phenomenon is called ***fluorescence.*** Such substances which emit radiations during the action of stimulating light are called ***fluorescent substances***. In fluorescence, it is essential for light to be absorbed before it is re-emitted. This distinguishes it from Tyndall, Rayleigh scattering and Raman effect. Fluorescence stops practically when the exciting light is shut off and this distinguishes it from phosphorescence, in which the emission continues for a short time even after the incident light is shut off.

According to Stokes (1852) the radiation emitted in fluorescence has a greater wavelength, *i.e.*, lower energy, than the exciting radiation, *i.e.*, the light originally absorbed. A few examples are known of anti-Stokes behaviour when the fluorescent radiation has a higher energy than the absorbed radiation. C.V. Raman observed this behaviour with substances such as carbon tetrachloride, benzene, when illuminated by radiation of wavelength 4500 Å, which is not supposed to be absorbed, but scattered by molecules of carbon tetrachloride and benzene.

[I] Resonance Fluorescence

An interesting case is known in which the atoms do not possess vibrational energy, they then exhibit what is known as ***resonance fluorescence,*** *i.e.,* the fluorescent light has the same frequency as that of the incident radiation. For example, if mercury vapour with atoms in the normal ($^1S_0$) state is exposed to ultraviolet light it will absorb resonance radiation of wavelength 2537 Å, and is converted into the excited state, *i.e.*, $^3P_1$.

$$Hg(^1S_0) + h\nu \longrightarrow Hg^*(^3P_1)$$

$$Hg^*\,(^3P_1) \longrightarrow Hg(^1S_0) + h\nu$$

If the pressure of the vapour is low, the collisions are not too frequent and the electrons in the excited atom will return to its normal level and emit the same radiation 2537 Å in a very short interval of time varying from 10^{-7} to 10^{-8} sec.

The reason for the above fact may be understood from figure (4) which shows a number of vibrational levels in each of the two electronic states of the molecule. Before absorption of light, most of the molecules are in their lowest ($V = 0$) vibrational level in the ground state, *i.e.*, S_0. Upon absorption of radiation, the molecules will occupy several of the vibrational levels of the excited electronic state as shown in the figure. During the 10^{-8} sec life of the excited state *i.e.*, S_1, some of the vibrational energy may be lost by collisions with other molecules, especially in solutions. When excess energy is emitted, transition will occur to various vibrational levels of the ground state. In several cases, the energy of the fluorescent radiation will be less and so its wavelength will be greater than that of the exciting radiation.

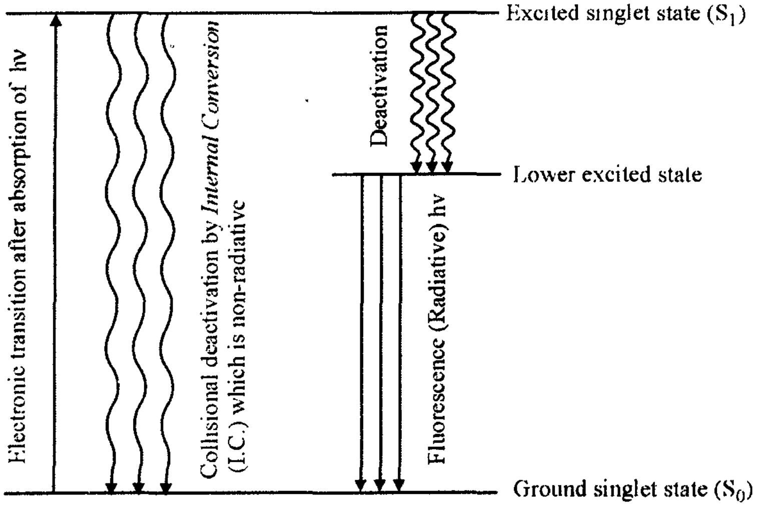

Excited singlet state (S_1)
Electronic transition after absorption of hν
Collisional deactivation by *Internal Conversion* (I.C.) which is non-radiative
Deactivation
Lower excited state
Fluorescence (Radiative) hν
Ground singlet state (S_0)

Fig. 4. Energy diagram for fluorescence.

[II] Sensitized Fluorescence

There are many substances which are non-fluorescent. But, when they are mixed with a fluorescent substance, they begin to exhibit fluorescence, when exposed to radiations. This phenomenon is known as *sensitized fluorescence.* For example, thallium is non-fluorescent. But, when it is mixed with Hg vapours and exposed to radiations of wavelength 2537Å, thallium shows fluorescence. This is explained as follows :

Step 1 : $\underset{\text{(Normal)}}{\mathrm{Hg}} + \underset{\text{(Absorbed radiation)}}{h\nu} \longrightarrow \underset{\text{(Excited)}}{\mathrm{Hg}^*}$

Step 2 : $\underset{\text{(Excited)}}{\mathrm{Hg}^*} + \underset{\text{(Normal)}}{\mathrm{Tl}} \longrightarrow \underset{\text{(Normal)}}{\mathrm{Hg}} + \underset{\text{(Excited)}}{\mathrm{Tl}^*}$

Step 3 : $\mathrm{Tl}^* \longrightarrow \mathrm{Tl} + \underset{\text{(Emitted radiation)}}{h\nu}$

[III] Examples of Fluorescence

Fluorescence is exhibited by many substances. Among them are fluorite, CaF_2 *(the name fluorescence originates from it)*, uranium glass, petroleum, solutions of dyestuffs as eosin, fluorescein, quinine sulphate, chlorophyll, vapours of sodium, iodine and acetone etc. Even simpler organic compounds as hydrocarbons (paraffins and olefines) have been found to fluoresce in ultraviolet region. Acetone absorbs 2700 Å corrsponding to $C=O$ group and emits blue fluorescence and similar is the case with aldehydes and other ketones.

Among inorganic substances there are only few instances such as uranium compounds and rare earths which show fluorescence. Fluorescence which is very marked with nitrogen peroxide in blue light (4920 to 4550Å) becomes much weaker in violet light (4550 to 3650Å) and practically vanishes at or beyond 3650 Å. When leaves are strongly illuminated in presence of oxygen, they emit fluorescent light with an intensity that changes with time of irradiation. The explanation of this has been given. According to Franck, Wood, during dark periods, the chlorophyll absorbs plant acids. On illumination, these plant acids use the energy absorbed by chlorophyll either for photosynthesis or for photo-oxidation.

[IV] Quenching of Fluorescence

When a photochemically excited atom has a chance to undergo collision with another atom or molecule before it fluoresces the intensity of fluorescent radiation may be diminished or stopped. This process is known as ***quenching of fluorescence.*** The fluorescence of gases and vapour is usually quenched when the total gas pressure exceeds a few millimeters of mercury, at which the pressure collisions between the excited molecules and other take place at time intervals shorter than 10^{-8} sec. The quenching may be caused by a foreign gas different from the fluorescing gas. Transfer of energy is facilitated when both types of molecules have the same energy level because of resonance. Inert gases, N_2, H_2 and O_2 act as quenchers. The thiocyanate, iodide, bromide and the chloride ions possess a marked quenching effect. The fluorescence of molecules may sometimes be quenched by the foreign molecules including dissociation on collision with the excited molecule. The quenching action of helium on the fluorescence of iodine is of this kind. Quenching of fluorescence occurs appreciably in a liquid medium because the collisions are frequent.

[V] Applications of Fluorescence

Fluorescence had found many applications of practical and industrial uses. Some of the applications are :

(1) ***In fluorescent tubes*** : In this, use is made of the fact that many inorganic solids also fluoresce. The modern tubular lights in which a mercury arc gives a large proportion of ultraviolet light is made in the tube coated internally with fluorescent salts giving visible light, with a distribution of intensity not far different from daylight.

(2) ***In fluorescent dyes and paints*** : Different types of dyes, paints and glasses exhibit characteristic fluorescent colours which make the substances nice to look at. The fluorescence of eye lens is excited by rays between 2500 Å and 4000 Å.

(3) ***In use of fluorescent microscope*** : It has been developed for biological purposes and it is based on the principle that almost all organic substances can be stimulated by visible or ultraviolet light.

(4) ***In television*** : It is based on the phenomenon of photoelectric effect. The cathode stream has to be made visible in cathode ray tube. This can be done by addition ZnS to which a little Ni is added to cut off the phosphorescence, otherwise the picture would be blurred.

(5) ***In analysis*** : The characteristic fluorescence of various substances when exposed to ultra-violet light provides a means of analysis. The intensity of fluorescence has been used for

quantitative analysis. Concentration of riboflavin (Vit. B_2) in chloroform has been examined by this method. Again fluorescence produced by X-rays falling on a screen of barium platinocyanide or other material is the principle of the fluoroscope used in X-ray diagnosis.

(6) ***In industry*** : Many substances by absorption of ultra-violet light exhibited fluorescent colours, a property which was made the basis of testing and identifying the materials. In rubber industry, ultra-violet rays might be used for checking the purities of ZnO, lithopone, oils, accelerators etc, and for the detection of errors in mixings due to mistakes in the incorporation of the ingredients.

Problem 8. ***Write an explanatory note on phosphorescence.*** **(Meerut 2007, 05)**

When a substance especially solid is irradiated by light, it begins to emit light, and when the light is shut off, the emission continues. The time interval for this emission may be from 10^{-2} second to hours or even days. This phenomenon is known as phosphorescence.

Phosphorescence is derived from phosphorous which glows in the dark, although it is not strictly phosphorescent. In fact, phosphorescence is best looked upon as slow fluorescence or phosphorescence of long duration.

[I] Characteristics of Phosphorescence

Some characteristics of phosphorescence are as follows :

(i) This phenomenon occurs even after the incident light is shut off.

(ii) This phenomenon is caused mainly by the ultraviolet and violet parts of the spectrum.

(iii) The time for which light is emitted from phosphorescent substances depends upon the nature of substance and sometimes on temperature changes.

(iv) Different colours may be obtained by mixing different phosphorescent substances.

(v) Phosphorescence is exhibited mainly by solids.

(vi) The magnetic and dielectric properties of phosphorescent substances are different before and after illumination.

[II] Mechanism of Phosphorescence

Phosphorescence is caused by UV and visible parts of spectrum. When an incident light falls on a phosphorescent substance, its

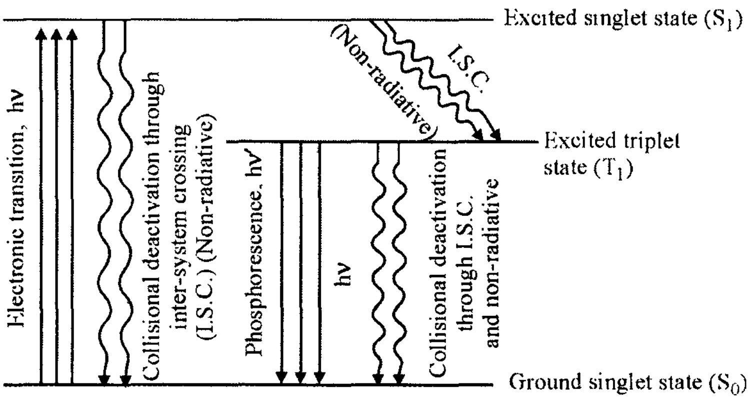

Excited singlet state (S_1)
Electronic transition, hv
Collisional deactivation through inter-system crossing (I.S.C.) (Non-radiative)
(Non-radiative)
I.S.C.
Excited triplet state (T_1)
Phosphorescence, hv'
hv
Collisional deactivation through I.S.C. and non-radiative
Ground singlet state (S_0)

Fig. 5. Energy diagram for phosphorescence.

molecules absorb energy $h\nu$ and get excited from S_0 state to S_1 state (Fig. 5). These excited molecules can return to S_0 state but through the following transitions :

(1) S_1 to T_0 : The excited molecule returns directly to ground state. Under such condition, fluorescence takes place.

(2) S_1 to T_1 : Under certain conditions, it is also possible that excited molecules may return to lower excited state through *inter system crossing* (ISC) which is non-radiative.

(3) T_1 to S_0 : The chances of returning of the molecules from T_1 *to* S_0 are very poor. Hence, the molecules stay in T_1 state for longer time. This stay is called *time lag*. The molecules which succeed in passing back to S_0 emit radiations and thus phosphorescence occurs. This emission of radiation, *i.e.*, phosphorescence, will take place very slowly and, hence, persists for some time. The frequency of phosphorescent light will be lower than that of incident light. So, we can say that there is no essential difference between phosphorescence and fluorescence, except that phosphorescence is a delayed type of fluorescence. This mechanism of phosphorescence has been confirmed by ESR spectroscopy.

[III] Examples of Phosphorescence

It is mostly observed in case of solids. In phosphorescence, the emission can only occur when the energy is taken from the surrounding medium according to Perrin. This leads to a delay in the electron jump by the action of the medium, which tries to keep the electron fixed in their neighbourhood in some sort of loose binding and this bond breaks with the help of thermal energy of the medium. The electron then returns with the accompaniment of phosphorescence and that is why phosphorescence does not occur in the gaseous state or in liquids. However, short after glow has been observed in denser medium, it has been seen to increase with the increase in the viscosity of the medium. These facts are confirmed further that lowering of temperature, as in the case of freezing of liquids, is helpful in producing phosphorescence. However, excessive cooling slows down the emission and at liquid air temperature, the emission may be completely cut off.

Phosphorescence is observed in solids because of greater difficulty in motion. It is found that if fluorescent substances are mixed by fusion with boric acid and are cooled, the masses which are formed then phosphoresce. The most common examples are of alkaline earth sulphides in which an addition of a trace of heavy metal enhances the phosphorescence.

Problem 9. ***Mention the factors which affect fluorescence and phosphorescence.***

The various factors which affect fluorescence and phosphorescence are as follows :

(i) All molecules cannot exhibit fluorescence and phosphorescence. Only those molecules exhibit these phenomena which are able to absorb ultraviolet or visible radiations. In general, the greater the absorbancy of a molecule, the more intense is its luminescence. On this basis, we can say that molecules having conjugated double bond (π-bonds) are particularly suitable for this study. Aliphatic and saturated cyclic organic compounds are not, however, suitable.

(ii) Substituents often show a marked influence on fluorescence and phosphorescence of molecules. Though there are no rigid rules, but some generalities are as follows.

(a) Electron withdrawing groups like $—COOH$, $—NO_2$, $—N=N—$ and halides decrease or even destroy fluorescence.

(b) Electron-donating groups like $—NH_2$ and $—OH$ often increase fluorescence. Groups like $—SO_3H$, NH_4^+ and alkyl groups do not have much effect on fluorescence and phosphorescence.

(c) If a high atomic number atom is added to a π-electron system, it decreases fluorescence but increases phosphorescence.

(iii) The pH also has a marked influence on the fluorescence of compounds, *e.g.*, a neutral or alkaline solution of aniline shows fluorescence in the visible region. However, in acidic solution, the visible fluorescence disappears. Aniline, however, shows fluorescence in UV region regardless of pH.

Problem 10. ***Mention the similarities and dissimilarities between fluorescence and phosphorescence.***

[I] Similarities

(i) Both these phenomena are caused by UV and visible parts of the spectrum.

(ii) These are regarded as the secondary processes resulting from the primary process of absorption of a quantum of light (UV and visible) by an atom or molecule.

(iii) Both these phenomena are considerably affected by the substituents in molecule. Generally, electron-donating groups enhances and electron-withdrawing groups destroy the phosphorescence and fluorescence.

[II] Dissimilarities

S. No.	Fluorescence	Phosphorescence
1.	It is shown by gases, liquids and solids. No fluorescence will be observed in gases unless the pressure is low.	It is exhibited mainly by solids.
2.	It is instantaneous and starts within 10^{-6} to 10^{-4} second of absorption of UV or visible light. It stops as soon as incident light is cut off. Thus, life-time of fluorescence is very short.	Substances showing phosphorescence re-emit excess radiation within 10^{-4} to 20 sec or longer after the incident light absorption. Thus, life-time of phosphorescence is much longer than fluorescence. It does not stop as soon as the incident light is cut off.
3.	The extent of fluorescence depends upon the nature of the solvent and the presence of certain anions in solution. So, thiocyanate, bromide and iodide anions show a marked quenching effect.	The time for which the radiation is emitted from phosphorescent substance depends upon the nature of substance and sometimes on the temperature changes.

4.	Fluorimetry is comparatively simple and finds wider applications.	Phosphorescence is more complicated experimentally than fluorescence and, therefore, phosphorimetry finds limited applications.
5.	Fluorimetry is less sensitive than phosphorimetry.	Phosphorimetry is more sensitive than fluorimetry.
6.	Scattering problems are more severe in fluorimetry.	Scattering problems do not exist in phosphorimetry.
7.	Quantum efficiency (ϕ) in fluorescence is the ratio of the number of photons of luminescent radiation to the number of photons absorbed from the stimulating light upon a fixed wavelength of the latter. The ϕ of fluorescence increases proportionally to the wavelength of absorbed radiation. After reaching maximum, the ϕ drops rapidly to zero upon further increase in λ In fluorimetry, the quenching poses some serious problems.	The quantum efficiency much more for phosphorescence than for fluorescence. The reason for this is that phosphorimetric determinations are carried out at 77K whereas the fluorimetric determinations are carried out at about 300K. One more advantage for the low temperatures (*i.e.*, 77K) in phosphorimetry is that the quenching does not pose a serious problem as in fluorimetry.

NUMERICAL PROBLEMS

Problem 1. ***Calculate the transmittance, absorbance and absorption coefficient of a solution which absorbs 90% of a certain wavelength of light beam passed through a 1 cm cell containing 0.25M solution.***

Sol. It is given that

$$I_{abs} = 0.90\,I_0; \quad x = 1 \text{ cm}; c = 0.25 \text{ M}$$

$$\therefore \qquad I_t = I_0 - I_{abs} = I_0 - 0.90\,I_0 = 0.10\,I_0$$

$\therefore$ Transmittance,

$$T = \frac{I_t}{I_0} = \mathbf{0.10}$$

Absorbance,

$$A = -\log\frac{I}{I_0} = \log\frac{I_0}{I} = \log\frac{1}{0.1} = \mathbf{1}$$

Applying Beer's law, we have

$$\log \frac{I_t}{I_0} = -\varepsilon' cx$$

i.e., $\log 0.10 = -\varepsilon' \times 0.25 \times 1$

or $-1 = -\varepsilon' \times 0.25$

or $\varepsilon' = \mathbf{0.4\ L\ mol^{-1}\ cm^{-1}}$

Problem 2. ***A certain substance in a cell of length l absorbs 10% of the incident light. What fraction of the incident light will be absorbed in a cell which is five times long?***

Sol. In the first case, $I_{abs} = 0.10\, I_0$ so that $I_t = 0.90\, I_0$

or $$\frac{I_t}{I_0} = 0.90$$

$$\log \frac{I_t}{I_0} = -k'l, \quad i.e., \quad \log 0.90 = -k'l$$

or $$k' = \frac{0.0458}{x}$$

In the second case, $x = 5l$ so that

$$\log \frac{I_t}{I_0} = -k' \times 5l = -\frac{0.0458}{l} \times 5l = -0.2290$$

or $$\log \frac{I_t}{I_0} = \bar{1}.7710$$

i.e., $$\frac{I_t}{I_0} = 0.5902 \quad \text{or} \quad I_t = 0.5902\, I_0$$

$$\therefore \quad I_{abs} = I_0 - I_t = I_0 - 0.5902\, I_0 = 0.4098\, I_0$$

$$= \mathbf{40.98\%\ of\ I_0}$$

Problem 3. ***In the photochemical decomposition (photolysis)*** $2HI \longrightarrow H_2 + I_2$ ***with light at*** $\lambda = 253.7$ ***nm, absorption of*** **3070 J** ***of energy decomposed*** 1.30×10^{-2} **mol** ***HI. What is the quantum yield, Φ of the reaction?***

Sol. The energy of the 253.7 nm quantum is $E = h\nu = (6.63 \times 10^{-34}\ \text{Js})\ (3.00 \times 10^{8}\text{m s}^{-1})/(253.7 \times 10^{-9}\ \text{m}) = 7.83 \times 10^{-19}\text{J}$. The HI has absorbed $N = 3070/7.83 \times 10^{-19} = 3.92 \times 10^{21}$ quanta or $3.92 \times 10^{21}/6.02 \times 10^{23} = 6.51 \times 10^{-3}$ einstein. The quantum yield,

$$\Phi = \frac{\text{No. of moles reacted}}{\text{No. of Einsteins absorbed}} = \frac{1.30 \times 10^{-2}}{6.51 \times 10^{-3}} = 1.99 \approx \mathbf{2.0}$$

Problem 4. ***Radiation of wavelength* 2500Å *was passed through* 10 *mL oxalic acid solution taken in a cell. The concentration of oxalic acid decreased from* 0.05 *to* 0.04 *molar due to the absorption of* 80J *radiant energy. Calculate the quantum efficiency for the photochemical decomposition of oxalic acid at* 2500Å.**

Sol. Energy associated with 2500Å radiation

$$= \frac{11.97 \times 10^5}{2500} \text{ kJ}$$

Energy of radiation $= 80 \text{ J} = 0.08 \text{ kJ}$

$\therefore$ Number of einsteins absorbed during experiment

$$= \frac{0.08 \times 2500}{11.97 \times 10^5} = 0.000167$$

Decrease in concentration of oxalic acid

$$= 0.05 - 0.04 = 0.01 \text{mol L}^{-1}$$

$$= \frac{10 \times 0.01}{1000} = 0.0001 \text{ mole}$$

$$\therefore \text{ Quantum efficiency, } \phi = \frac{\text{Number of moles decomposed}}{\text{Absorbed number of einsteins}}$$

$$= \frac{0.0001}{0.000167} = \mathbf{0.598.}$$

Problem 5. ***Hydrogen iodide decomposes when irradiated with radiation of wavelength* 2820Å, *the quantum efficiency being* 2. *Calculate the number of millimoles of HI undergoing decomposition with each erg of energy absorbed.***

Sol. Energy per quantum associated with radiation of wavelength 2820Å

$$= h\nu = \frac{hc}{\lambda}$$

$$= \frac{(6.626 \times 10^{27} \text{ erg s})\ (3 \times 10^{10} \text{ cm s}^{-1})}{2820 \times 10^{-8} \text{ cm}}$$

Number of quanta per erg of this radiation

$$= \frac{2820 \times 10^{8} \text{ cm}}{(6.626 \times 10^{27} \text{ erg s})\ (3 \times 10^{10} \text{ cm s}^{-1})}$$

Quantum efficiency,

$$\phi = \frac{\text{No. of molecules reacting}}{\text{No. of quanta of energy absorbed}}$$

or $$2 = \frac{\text{No. of molecules reacting}}{141.9 \times 10^9}$$

$\therefore$ No. of molecules reacting $= 2 \times 141.9 \times 10^9$

$$\text{No. of moles reacting} = \frac{2 \times 141.9 \times 10^9}{6.023 \times 10^{23}} = \mathbf{47.1 \times 10^{-14}}$$

$$\text{No. of millimoles reacting} = 47.1 \times 10^{-14} \times 10^3 = \mathbf{47.1 \times 10^{-11}}.$$

Problem 6. ***For a photochemical reaction, A $\longrightarrow$ B, 1 × 10^{-5} moler of B was formed on absorption of 6.62 × 10^7 erg at 3600Å. Calculate the quantum efficiency.***

Sol. Number of molecules reacting

$$= 1 \times 10^{-5} \times 6.023 \times 10^{23} = \mathbf{6{\cdot}023 \times 10^{18}}$$

$$\therefore \text{ No. of quanta absorbed} = \frac{\text{Total energy absorbed}}{\text{Energy of one quantum}}$$

$$= \frac{6.62 \times 10^7 \text{ erg}}{h\nu} = \frac{6.62 \times 10^7}{\frac{hc}{\lambda}} = \frac{6.62 \times 10^7 \lambda}{hc}$$

$$= \frac{6.62 \times 10^7 \times 3600 \times 10^{-8}}{6.62 \times 10^{-27} \times 3 \times 10^{10}} = 1.2 \times 10^{19}$$

$$\therefore \text{ Quantum efficiency} = \frac{\text{No. of molecules reacting}}{\text{No. of quanta absorbed}}$$

$$= \frac{6.023 \times 10^{18}}{1.2 \times 10^{19}} = \mathbf{0.5016}$$

Problem 7. ***The quantum yield of the reaction***

$$\mathbf{H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)}$$

is 1 × 10^6 with a wavelength 480 nm. Calculate the number of moles of HCl(g) produced per joule of radiant energy absorbed.

Sol. Energy absorbed per mole

$$= \frac{Nhc}{\lambda}$$

$$= \frac{1.196 \times 10^8}{\lambda \text{ (in cm)}} \text{ erg mole}^{-1}$$

$$= \frac{1.196 \times 10^8}{10^7 \times \lambda} \text{ joule mole}^{-1}$$

$$\therefore \qquad E = \frac{1.196 \times 10^8}{4800 \times 10^{-8} \times 10^7} = 2.492 \times 10^5 \text{ J mole}^{-1}$$

Now, $$\phi = \frac{\text{No. of moles reacted}}{\text{No. of einsteins absorbed}}$$

Number of moles reacted = $\phi \times$ No. of einsteins absorbed

$\therefore$ No. of moles of HCl formed = 2 × No. of moles of H_2 or Cl_2 reacted

$$= 2 \times \phi \times \text{No. of einsteins absorbed}$$

$$= 2 \times 1 \times 10^6 \times \left(\frac{1}{2.492 \times 10^5}\right)$$

$$= \mathbf{8.02 \text{ moles}}$$

EXERCISE

[I] Short Answer Type Questions

1. Write a short note on Stark-Einstein's law of photochemical equivalence. **(Meerut 2007, 06)**
   [For answer, please see problem 2]
2. Mention Jablonski diagram. **(Meerut 2005)**
   [For answer, please see problem 5]
3. Mention the reasons for low and high quantum yields. **(Meerut 2007, 06)**
   [For answer, please see problem 3]
4. Describe the differences between photochemical and thermal reactions.
   [For answer, please see problem 1]
5. Explan the term fluorescence. **(Meerut 2007)**
   [For answer, please see problem 7]
6. Explain the term phosphorescence. **(Meerut 2007)**
   [For answer, please see problem 8]
7. Write a short note on photosensitization.
   [For answer, please see problem 6]
8. What are singlet and triplet states ?
   [For answer, please see problem 4]
9. Mention the characteristics of singlet and triplet states.
   [For answer, please see problem 4]
10. Mention the differences between fluorescence and phosphorescence.
    [For answer, please see problem 10]
11. Explain the factors which affect fluorescence.
    [For answer, please see problem 9]

12. Calculate the energy of an einstein of radiation of wave length 253.7 nm. **[Ans. 471.9 kJ]**
[For answer, please see numerical problem 2]

[II] Very Short Answer Type Questions

1. Define Beer's law. **(Meerut 2006)**
[For answer see problem 2]
2. Define Lambert's law. **(Meerut 2006)**
[For answer see problem 2]
3. Define Einstein's law of photochemical equivalence. **(Meerut 2007, 06, 05)**
[For answer see problem 2]
4. Define inter-system crossing.
[For answer see problem 5]
5. What is internal conversion ?
[For answer see problem 5]
6. Define an einstein.
[For answer see problem 2]
7. Mention a reaction in which the quantum yield is high and low.
[For answer see problem 3]
8. What are photochemical reactions ?
[For answer see problem 1]

❑❑❑

UNIT-4

PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

Optical activity, polarisation, Clausius-Mosotti equation, orientation of dipoles in an electric field, dipole moment, induced dipole moment, measurement of dipole moment–temperature method and refractivity method, dipole moment and structure of molecules, magnetic properties of substances, paramagnetism, diamagnetism and ferromagnetics.

PROBLEMS

Problem 1. ***Explain the terms, plane of polarisation, optically active substance and optical activity. How is angle of rotation determined? Explain how optical activity is used to decide the constitution of a compound ?*** **(Meerut 2006, 05)**

[I] Plane of Polarisation, Optically Active Substance and Optical Activity

Ordinary light consists of rays of different wavelengths vibrating in all directions perpendicular to the direction of propagation. If the vibrations are by any means restricted to one plane only, it is called ***plane polarized light*** and the plane along which vibrations are taking place is known as ***plane of polarization***. The device that brings about polarization of light is called a ***polariser***. When an ordinary ray of light is passed through a nicol prism the emerging rays vibrate only in one plane. Some substances possess a special property by virtue of which they are capable of rotating the plane of polarised light. *So, those substances which can rotate the plane of polarised light are said to be* ***optically active substances*** *and this property is called* ***optical activity.***

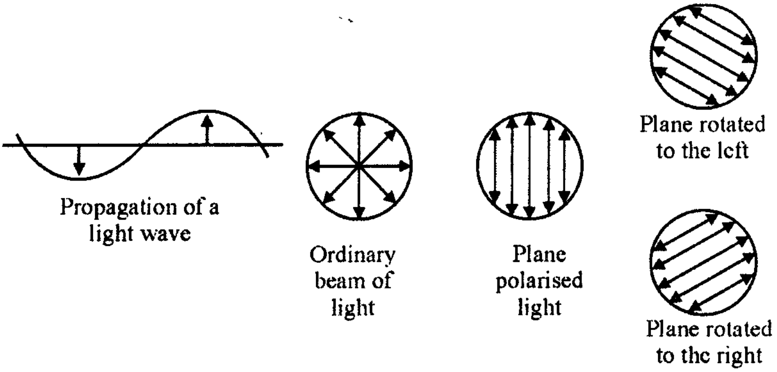

Plane rotated to the left
Propagation of a light wave
Ordinary beam of light
Plane polarised light
Plane rotated to the right

Fig. 1.

[II] Optical Rotation, Specific Rotation and its Determination

The optical rotation of the plane of polarised light produced by a solution is determined by means of a polarimeter. It depends on:

(i) Amount of the substance in the tube

(ii) Length of the solution to be examined

(iii) Temperature of the experiment

(iv) Wavelength of light used.

The optical rotation α (in degrees) is given by the equation,

$$\alpha = [\alpha]_D^t \, l \, (m/V)$$

where l is the length of the column in decimetres through which the light passes, m is the mass of the optically active substance in grams occupying a volume of V ml and $[\alpha]_D^t$ is a constant which depends upon the nature of the substance, temperature (t) and wavelength (λ) of the light and is called the ***specific rotation*** of the substance. It is characteristic of a substance under given conditions of temperature and wavelength of light used. As D-light of sodium flame is generally used, the specific rotation may be expressed as :

$$[\alpha]_D^t = \frac{\alpha V}{lm}$$

Specific rotation is defined as, *"the angle of rotation of the plane of polarised light by a liquid, which in a volume of* 1 *ml contains* 1 *gram of the active substance when the length of the column through which the light passes is one decimetre."*

If the active substance is used as such then we have

$$[\alpha]_D^t = \frac{\alpha}{l\rho} \qquad (\because \ V/m = 1/\rho)$$

where ρ is the density of the substance.

If the substance is in solution, the concentration must be taken into account and the equation may be put as,

$$[\alpha]_D^t = \frac{100\alpha}{lc}$$

where c is the number of grams of the substance in 100 ml of the solution.

The specific rotation of sucrose solution at 20°, using sodium light, is + 66.5° which can be represented as :

$$[\alpha]_D^{20} = +66.5°$$

The sign attached with the angle of rotation signifies the direction of rotation. Negative sign (–) shows that the rotation is towards the left, while positive sign (+) shows that the rotation is towards the right.

[III] Measurement of rotatory power

The instrument used for measuring the angle of rotation of plane of polarised light is called ***polarimeter*** (figure 2). It consists of two Nicol prisms mounted on the axis of the instrument. The first prism called ***polariser*** is fixed and the other called ***analyser*** can be rotated about the axis of the instrument. A tube containing an optically active liquid or a solution of an optically active substance is placed in the path of light between the two Nicols. The length of the tube is definite varying from 5 cm to 25 cm.

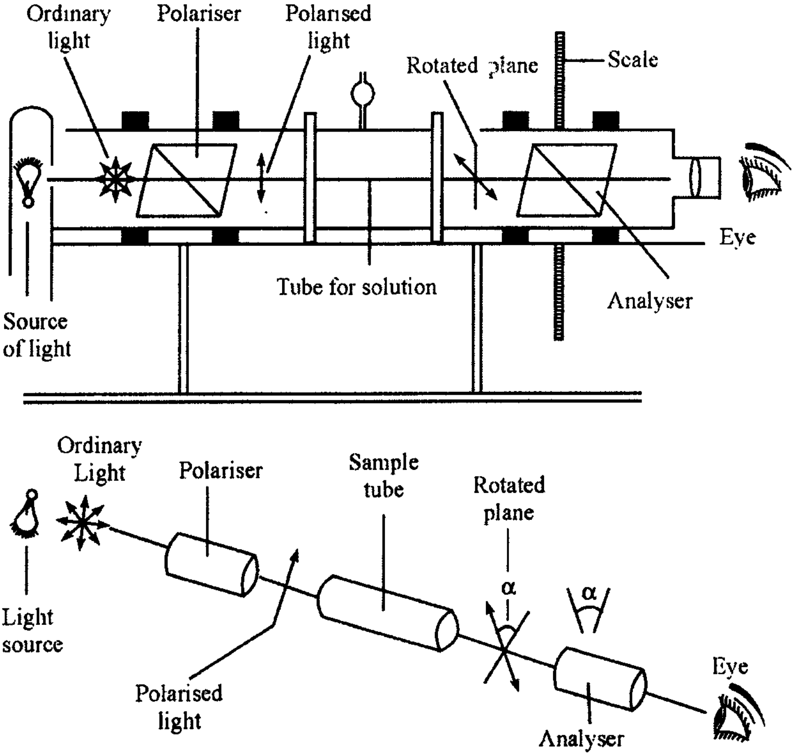


Fig. 2. Polarimeter

A beam of monochromatic light usually sodium light is passed through the polarimeter without the tube containing the liquid. The light gets polarised by the first Nicol and then falls on the second which is gradually rotated so as to cut out the light completely. The reading on the scale is noted. It corresponds to zero reading.

The tube containing the liquid is then inserted. On looking through the polarimeter, the field will appear bright, as the optically active substance has rotated the plane of polarised light through a certain angle. The analyser is turned towards the right or left as may be required so as to get the complete darkness again. The reading of the scale is noted. The difference between this and the first reading gives the required angle of rotation.

[IV] Optical Isomerism

Many organic compounds having similar chemical and physical properties behave differently towards polarised light and rotate the plane of polarisation towards right, left or cause no optical activity. *When the same compound behaves differently towards polarised light, it is said to exhibit optical isomerism and different forms are known as optical isomers.*

(i) Isomer which is capable of rotating the plane of polarised light towards right (clockwise) is said to be dextro-rotatory or *d*-form.

(ii) Isomer which is capable of rotating the plane of polarized light towards left (anti-clockwise) is called laevo rotatory or *l*-form.

(iii) Isomer which does not rotate the plane of polarized light at all is called optically inactive (meso, racemic or *dl*-form).

Several organic compounds, *e.g.*, lactic acid, malic acid, glucose etc. show optical isomerism. Pasteur (1836) started his work on tartaric acid and made the following observations :

(i) The tartaric acid obtained from grape juice was optically active and is dextro-rotatory.

(ii) The same acid when recovered from mother liquor left after the purification of tartaric acid was inactive, *i.e.*, racemic tartaric acid.

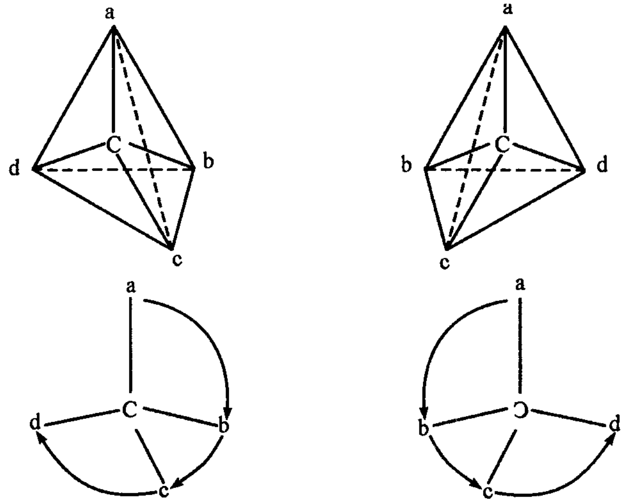
He prepared sodium ammonium salts of both the above acids. He observed crystals of *d*-tartaric acid were all alike and possessed hemihedral facets, while crystals of racemic tartaric acid had two types of crystals, one having facets towards right like *d*-form. Other type of crystals are mirror image of first, *i.e.*, having facets towards left. He separated two kinds of crystals obtained from racemic tartaric acid by hand picking. He dissolved them in water separately and observed their rotations.

[V] Explanation of Optical Activity

The explanation of optical activity was put forward simultaneously but independently by van't Hoff and Le Bel in 1874. According to them, the four valencies of carbon are directed towards the four corners of a regular tetrahedron, at the centre of which carbon atom is situated. If there are four different atoms or groups, *a*, *b*, *c* and *d* attached to four corners of a tetrahedron, then two different arrangements are possible. These two arrangements are not superimposable and bear the mirror image relationship.

A carbon atom which is attached to four different atoms or groups is called an ***asymmetric carbon atom*** *and the molecule containing it is called on* ***asymmetric molecule.*** A molecule is symmetrical if it possesses a plane of symmetry. A plane of symmetry is one which divides a molecule into two halves in such a way that one half is the mirror image of the other or if a line from any atom or group on one side of the plane is drawn perpendicular to the plane and extended to an equal distance on the other side meets a similar atom or group at its end.

Consider a carbon atom having four different groups or atoms *a*, *b*, *c* and *d* attached to its valencies at the four corners of the



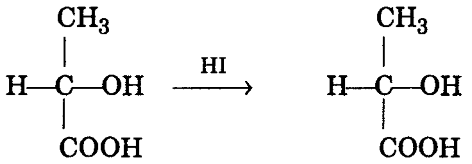
(i) Clockwise arrangement of groups a, b, c, d

(ii) Anticlockwise arrangement of groups a, b, c, d

Fig. 3.

regular tetrahedron. Two arrangements are possible which are related to one another as an object to its mirror image. They will not be super-imposable upon each other. The arrangement of groups is different in figures 3 (i) and (ii). If for example, one has to go from *a* to *d* through *b* and *c*, one will have to go in clockwise direction in form (i) and in anti-clockwise direction in form (ii). On super-imposing structures (i) and (ii), groups *a*, *c* and *b* will overlap each other but group *d* from each of the forms will go on opposite sides. So, the two models show two isomeric spatial arrangements or different configurations. The compounds represented by forms (i) and (ii) are called ***enantiomers*** or ***enantiomorphs*** (Greek : *enantio* = opposite; *morph* = form). Thus, optical isomerism is also referred to as ***enantiomerism***. It is true that generally compounds containing one or more asymmetric carbon atoms exhibit enantiomerism.

Optical isomerism shown by lactic acid disappears as soon as the molecule becomes symmetrical, *i.e.*, when converted into propionic acid. This clearly indicates that the molecule as a whole should be asymmetric. Hence, it is quite evident that the presence of asymmetric carbon atom is not sufficient to make a molecule optically active. So, optically activity shows the presence of an asymmetric carbon atom in a molecule.



$$\begin{array}{c} CH_3 \\ | \\ H-C-OH \\ | \\ COOH \end{array} \xrightarrow{HI} \begin{array}{c} CH_3 \\ | \\ H-C-OH \\ | \\ COOH \end{array}$$

Lactic acid (Asymmetric, as a whole optically active)

Propionic acid (Not asymmetric, as a whole optically inactive)

NUMERICAL PROBLEMS

Problem 1. ***A solution of an organic solute placed in a* 20 *cm polarimeter tube, produces a rotation of* + 38.73°. *The same tube containing pure solvent only has a rotation of* + 1.46°. *If the specific rotation of the solute is* 62.12°, *what is the concentration of the solute in the solution?***

Sol. $\alpha = (38.73° - 1.46) = 37.27°$

$$[\alpha]_D^t = 62.12, \; l = 20 \text{ cm} = 2 \text{ dm}$$

We know, $$[\alpha]_D^t = \frac{100\,\alpha}{lc}$$

or $$c = \frac{100 \times 37.27}{62.12 \times 2} = \mathbf{30\ g\ per\ 100\ ml}$$

Problem 2. 1 ***g of an organic substance when dissolved in 50 ml of water and placed in a 2 decimetre polarimeter tube produces a rotation of +2.676°. The rotation produced by distilled water in the same tube was + 0.016°. Calculate the specific rotation of the substance.***

Sol. Concentration of solution = 1 g in 50 ml = 2 g in 100 ml

$$[\alpha]_D^t = (2.676° - 0.016°) = 2.660°$$

We know, $$[\alpha]_D^t = \frac{100\alpha}{lc} = \frac{100 \times 2.660}{2 \times 2} = \mathbf{+\ 66.50°}$$

Problem 2. ***(i) What are polar and non-polar melecules ? (ii) What is dipole moment and mention its unit?*** **(Meerut 2007)**

[I] Polar and Non-Polar Molecules

A molecule is composed of positively charged nuclei and negatively charged electrons in such a way that the molecule as a whole remains electrically neutral. The arrangement of these charged particles is different for different molecules. There are two possibilities:

(i) When the centre of gravity of the positive charges in a molecule is exactly at the same point as that of the negatively charged electrons, it is called a ***non-polar molecule,*** *e.g.*, H_2, Cl_2, CO_2, CH_4, C_6H_6 etc.

(ii) When the centre of gravity of electrons does not coincide with that of positive nuclei, the molecule is called a ***polar molecule,*** *e.g.*, H_2O, NH_3, $CHCl_3$ etc. The molecule as a whole is neutral, so we have equal positive $(+q)$ and negative $(-q)$ charges separated by a certain distance (l) in a polar molecule. So, a polar molecule behaves like a small magnet and becomes dipolar. Therefore, it is called an ***electric dipole*** or simply a ***dipole*** (two poles). Sidgwick proposed that a dipole may be shown by an arrow with a crossed tail. The arrow (⟶) is placed parallel to the line of positive and negative charges and should be from positive end to negative end of the dipole, as shown in HCl molecule Fig. (4).

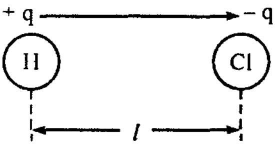


Fig. 4. Representation of dipole, where ***l*** **is the bond length.**

It can also be concluded that non-polar molecules do not have permanent dipoles, while polar molecules have permanent dipoles.

[II] Dipole Moment

The degree of polarity of a molecule can be expressed in terms of dipole moment. It is defined as, ***"the product of the magnitude of the charge (positive or negative) and distance between them (bond length)".*** If q is the charge at each end of the molecule and l is the distance between the positive and negative ends, the dipole moment ($\vec{\mu}$) is given by,

$$\vec{\mu} = q \times l$$

In a non-polar molecule, the distance l is zero as centres of gravity of positive and negative charges coincide, hence dipole moment is zero.

The dipole moment has a direction as well as a magnitude, *i.e.*, it is a vector quantity. It is frequently convenient to represent a dipole moment by an arrow showing the direction from the positive to the negative charge and the length of arrow represents the magnitude of dipole moment. Dipole moments being vectorial quantities, may be added vectorially.

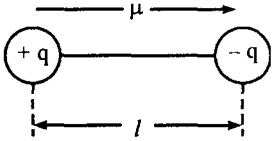


Fig. 5. Representation of dipole moment

The dipole moment arises due to the difference in the electronegativities of the two atoms held together by a chemical bond. In case of two or more bonds in a molecule, the net dipole moment will be the vector addition of dipole moments of chemical bonds. Each chemical bond has a definite dipole moment. The magnitude of dipole moment in a polar molecule depends on the difference in the electronegativities. The greater the difference in electronegativities, the greater is the dipole moment. Greater the dipole moment, greater is the degree of polarity of polar covalent bond between the two atoms.

[III] Unit of Dipole Moment

We know that,

Dipole moment (μ) = Electronic charge (q) × Bond length (l)

The charge is expressed in electrostatic unit (esu) and bond length in angstrom unit (1 Å = 10^{-8} cm). If an electron (charge = 4.8×10^{-10} esu), is assumed to be placed at a distance of 1 Å (= 10^{-8} cm), from an equal positive charge, then dipole moment (μ) of such a molecule is given by,

$$\mu = (4.8 \times 10^{-10} \text{ esu}) \times (10^{-8} \text{ cm}) = 4.8 \times 10^{-18} \text{ esu-cm}$$

The quantity 10^{-18} esu-cm is called one debye unit, denoted by D, *i.e.*, $1\ D = 10^{-18}$ esu-cm. So, $\mu = 4.8$ D.

In S.I. system, the electronic charge,

$$q = 1.602 \times 10^{-19}\ \text{C and } l = 10^{-10}\ \text{m, so,}$$

$$\mu = (1.602 \times 10^{19}\ \text{C}) \times (10^{-10}\ \text{m})$$

$$= 1.602 \times 10^{-29}\ \text{Cm} = 4.8\ \text{D}$$

$$\therefore \qquad 1\ \text{D} = 3.336 \times 10^{-30}\ \text{Cm}$$

Problem 3. ***Explain the following terms :***

(i) Electrical or distortion polarisation

(ii) Induced dipole moment

(iii) Polarisability

(iv) Molar polarisation

(v) Permanent dipole moment. **(Meerut 2006)**

[I] Electrical or Distortion Polarisation

Consider a non-polar molecule. When it is placed in an electric field between two charged poles, the latter will attract the electrons towards the positive pole, while the positive nuclei is attracted towards the negative pole. Thus, the positive and negative centres would no longer be coincident [Figure 6(a)]. *There will thus be an electrical distortion of the molecule to form an* ***electrical dipole.*** Such a distortion is termed ***distortion polarisation*** or ***electrical polarisation.***

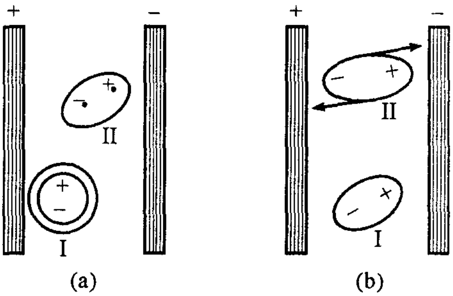


Fig. 6.

[II] Induced Dipole Moment

As soon as the electrical field as applied to a non-polar molecule is withdrawn, the distortion also disappears. The distortion polarisation thus produced is, therefore, an ***induced polarisation*** and the moment that the induced dipole would acquire during the application of the field is the ***induced dipole moment,*** μ_i.

[III] Polarisability

The induced dipple moment (μi) is directly proportional to the field strength, F. It is given by

$$\mu_i = \alpha \, . \, F$$

where the proportionality constant (α) is called the polarisability of the molecule. If $F = 1$, then $\alpha = \mu_i$.

So, the ***polarisability of the molecule*** *is a measure of the moment induced by a unit field.*

On the basis of electromagnetic theory, Clausius and Mosotti deduced the following relation between polarisability (α) and the dielectric constant (D) of a medium between the charged plates.

$$\frac{4}{3}\pi N\alpha = \frac{D-1}{D+2} \cdot \frac{M}{\rho} \qquad \ldots (1)$$

where N is Avogadro's number, M is molecular weight and ρ is the density of the substance.

[IV] Molar Polarisation

The right hand side of equation (1) is termed ***molar polarisation***. In a non-polar molecule, the polarisation is all induced. So, the induced molar polarisation (P_i) may be expressed as

$$P_i = \frac{4}{3}\pi N\alpha = \frac{D-1}{D+2} \cdot \frac{M}{\rho} \qquad \ldots (2)$$

P_i is the electrical distortion caused in one mole of a substance in a unit field. As N and α are independent of temperature, P_i will also be independent of temperature. Moreover, D is a dimensionless number and so the polarisation will be expressed in units of volume.

[V] Permanent Dipole Moment

Each of the polar molecules has a positive and a negative end. In the absence of an electical field, the molecules would be randomly oriented in all directions due to thermal effect. However, when such molecules are placed in an electric field between two charged plates, there will arise two effects. *Firstly,* the usual distortion of the positive and negative charges would occur giving rise to induced polarisation. *Secondly*, the field would tend to orient all the molecules in the direction of the field. If the molecules were stationary, these would be oriented at 180° to the direction of the field, the negative ends pointing towards the positive plate, as shown in figure 6.1 (*b*). This effect of the field on the molecules is called the ***orientation polarisation,*** P_0.

The molar polarisation, which is measured from dielectric constant, $\left[\frac{D-1}{D+2}\cdot\frac{M}{\rho}\right]$ is the sum of two effects, *viz.*, induced and orientation polarisations. The total molar polarisation is given by

$$P_t = P_i + P_0$$

and $$P_t = \frac{D-1}{D+2}\cdot\frac{M}{\rho}$$

$\therefore$ $$\frac{D-1}{D+2}\cdot\frac{M}{\rho} = P_i + P_0$$

or $$\frac{D-1}{D+2}\cdot\frac{M}{\rho} = \frac{4}{3}\pi N\alpha + P_0 \qquad \ldots (3)$$

The molar orientation polarisation (P_0) of a substance having a dipole moment (μ) was given by Debye and is expressed as

$$P_0 = \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \ldots (4)$$

where k is Boltzmann's constant.

It is thus clear that in a non-polar molecule ($\mu = 0$), there is no orientation polarisation and moreover, the orientation polarisation is inversely proportional to temperature. Thus, from equations (3) and (4), we have

$$P_t = \frac{D-1}{D+2}\cdot\frac{M}{\rho} = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \ldots (5)$$

Equation (5) is known as ***Debye equation.***

As the first term on the right hand side of equation (5) is a constant and μ is also constant for a given substance, equation (5) may be written as

$$P_t = \frac{D-1}{D+2}\cdot\frac{M}{\rho} = a + \frac{b}{T} \qquad \ldots (6)$$

where $a = \frac{4}{3}\pi N\alpha$ and $b = \frac{4}{9}\cdot\frac{\pi N}{k}\mu^2$

From equation (6), it is clear that the total molar polarisation varies linearly with $1/T$. It can be verified by plotting P_t against $1/T$ for several substances, as shown in figure (7). Figure (7) shows the linear plots for a gaseous non-polar molecule such as CH_4 ($\mu = 0$) and a gaseous polar molecule such as HCl with $\mu \neq 0$. For a non-polar molecule since $\mu = 0$, a plot of P_t and $1/T$ should give a straight line parallel to $1/T$ axis.

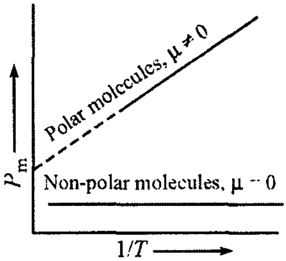


Fig. 7. Plot of P_t versus $1/T$ for gaseous polar and non-polar molecules.

Problem 4. *Mention the different methods for the determination of dipole moment.* **(Meerut 2007, 06, 05)**

A number of methods are available for determining the dipole moment. These are discussed as follows :

(1) Temperature Method : By determining the dielectric constant directly, the total polarisation (P_t) of a substance is obtained, M and ρ being determined separately. As seen from equation (6), we have

$$P_t = a + \frac{b}{T}$$

If total polarisations P_1 and P_2 are determined at two temperatures T_1 and T_2, respectively then

$$P_1 = a + \frac{b}{T_1} \quad \text{and} \quad P_2 = a + \frac{b}{T_2}$$

$$\therefore \qquad b = (P_1 - P_2)\left(\frac{T_1 T_2}{T_2 - T_1}\right) \qquad \dots (7)$$

The value of dipole moment, μ is easily calculated from that of b, *i.e.*,

$$b = \frac{4\pi N}{9k}\mu^2$$

$$\text{or} \qquad \mu = \sqrt{\left(\frac{9k}{4\pi N}\right) . b}$$

As $k = 1.3807 \times 10^{-16}$ erg K^{-1}, $\pi = 3.14$, $N = 6.023 \times 10^{23}$, we get

$$\mu = \sqrt{\left(\frac{9 \times 1.3807 \times 10^{-16} . b}{4 \times 3.14 \times 6.023 \times 10^{23}}\right)}$$

$$= 0.0128 \times 10^{-18} . \sqrt{b} \text{ e.s.u.-cm.}$$

So, knowing b from equation (7), we can calculate the dipole moment easily.

(2) Ebert's Method : Polar molecules in the gaseous state when subjected to an electric field will undergo both orientation and distortion polarisations. But when the same substance in the solid state is subjected to the same field, the orientation of molecules is not possible and only distortion polarisation will occur. Therefore, the total molar polarisation is given by

$$P_{\text{gas}} = P_i + P_0$$

$$P_{\text{solid}} = P_i$$

$\therefore$ Orientation polarisation, $P_0 = P_{\text{gas}} - P_{\text{solid}}$

or $$\frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) = P_{\text{gas}} - P_{\text{solid}}$$

or $$\mu = \sqrt{\left[\frac{9kT}{4\pi N}(P_{\text{gas}} - P_{\text{solid}})\right]} \quad \ldots (8)$$

As all the values of equation (8) are known, we can calculate the value of dipole moment.

(3) Dilute Solution Method : The Debye equation is applicable only to gaseous systems. In condensed systems (*i.e.*, solids and liquids), strong intermolecular interactions exist, so Debye equation cannot be applied. However, if measurements are carried out on dilute solutions of a polar molecule in a non-polar solvent, such as C_6H_6, CCl_4 etc., Debye equation can be applied for determining μ and α. The solute-solute and the solute-solvent interactions in dilute solutions can be eliminated by plotting molar polarisation (P_t) against mole fractions of solute and extrapolating the data to zero concentration.

Consider a dilute solution of a polar solute 2 in a non-polar solvent 1. The molar polarisation of the solution can be written as,

$$(P_t)_{1,2} = \frac{D_{1,2} - 1}{D_{1,2} + 2} \cdot \frac{M_a}{\rho_{1,2}}$$

where $$M_a = x_1 M_1 + x_2 M_2.$$

In the above equation, x_1 and x_2 are the mole fractions of the solvent and solute, respectively, M_a is the average molar mass of the solute-solvent system; $\rho_{1,2}$ is the density and $D_{1,2}$ is the dielectric constant of the solution. Supposing that the molar polarisation is directly proportional to respective mole fractions, we can write,

$$(P_t)_{1,2} = x_1 P_1 + x_2 P_2 = (1 - x_2) P_1 + x_2 P_2 \quad \ldots (9)$$

or $$(P_t)_{1,2} = P_1 + (P_2 - P_1)\, x_2$$

where P_1 and P_2 are the molar polarisations of solvent and solute, respectively.

Since a non-polar solvent has only distortion polarisation, which is not greatly affected by interactions between molecules, we can assume that P_1 has the same value in solution as in the pure solvent. So,

$$P_1 = \frac{D_1 - 1}{D_1 + 2} \cdot \frac{M_1}{\rho_1}$$

P_2 can be calculated from the re-arrangement of equation (9), *i.e.*,

$$P_2 = \frac{(P_t)_{1,2} - P_1\,(1 - x_2)}{x_2} = \frac{(P_t)_{1,2} - P_1\, x_1}{x_2}$$

The values of P_2 obtained from the above equation vary with x_2, presumably due to the solute-solute interactions. These interactions can be minimised by extrapolating the curve of P_2 against x_2 to zero concentration. Thus, $P_2{}^\circ$, *i.e.*, value of P_2 at infinite dilution can be obtained. If $P_2{}^\circ$ is known at different temperatures, its plot against $1/T$ can give the value of dipole moment (μ) of the solute.

(4) **Refractivity Method :** The induced polarisation, P_i is due to the distortion of the nuclei and electrons. On considering these two distortions separately, we may have

$$P_i = P_a + P_e$$

where P_a called the ***atomic polarisation*** is due to distortion of the nuclei and P_e called the ***electronic polarisation***, is due to the distortion of the electrons. So, the total polarisation, P_t is given by

$$P_t = (P_a + P_e) + P_0$$

Maxwell showed that for the same electromagnetic wave, the dielectric constant (*D*) of the medium and the refractive index (*n*) is related by the expression,

$$D = n^2.$$

So, the total polarisation $\frac{D-1}{D+2} \cdot \frac{M}{\rho}$ may be replaced by the molar refraction $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho}$. It is, however, not strictly so

The refractive index is measured with visible radiation of higher frequency, whereas the value of *D* is measured with long waves. The refractive index changes with wavelength. The Cauchy formula gives the correction for refractive index for lower frequency, as

$$n = n_\alpha + \frac{a}{\lambda^2}$$

where n is the refractive index at wavelength λ and n_α is the refractive index at very high wavelengths, a is a constant whose value may be determined from two measurements of n at known frequencies in the visible region. We shall thus replace D by n_a.

Moreover, in refraction only the electrons are affected by the radiation. Even when corrected for long waves, the refractive index gives the effect of the long waves on the electrons only and the nuclei remain unaffected. So, the molar polarisation given by $\frac{n_\alpha^2 - 1}{n_\alpha^2 - 2} \cdot \frac{M}{\rho}$, gives only the electronic polarisation (P_e), *i.e.*,

$$P_e = \frac{n_\alpha^2 - 1}{n_\alpha^2 + 2} \cdot \frac{M}{\rho}$$

The total molar polarisation,

$$P_t = \frac{D-1}{D+2} \cdot \frac{M}{\rho} = P_\alpha + \frac{n_\alpha^2 - 1}{n_\alpha^2 + 2} \cdot \frac{M}{\rho} + \frac{4\pi N}{9kT}\mu^2 \quad \ldots (10)$$

Equation (10) thus gives a method for determination of atomic polarisation, P_a. Dipole moment may be obtained from any of the previous method and then if D and n_a^2 be separately measured, their substitution will give us the value of P_a.

It has been found that for a large number of organic molecules the atomic polarisation P_a is relatively small as compared to the electronic polarisation, P_e. The former is nearly 5% of the latter. On this basis. equation (10) may be written as.

$$\frac{D-1}{D+2} \cdot \frac{M}{\rho} = 1.05 + \frac{n_\alpha^2 - 1}{n_\alpha^2 + 2} \cdot \frac{M}{\rho} + \frac{4\pi N}{9kT}\mu^2 \quad \ldots (11)$$

Thus, the values of dielectric constant and refractive index would give us the value of dipole moment, μ.

Problem 5. ***Describe the different applications of dipole moment.*** **(Meerut 2006, 05)**

(1) In determining molecular structures of substances :

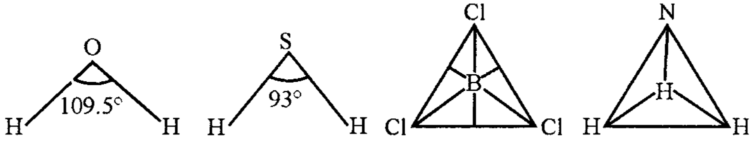
(a) Monoatomic molecules, like those of rare gases, have no dipole moment and are ***non-polar.***

(b) Diatomic molecules may be either polar or non-polar. Molecules of gases like O_2, N_2 etc. have $\mu = 0$, which indicates that the electron pairs bonding the constituent atoms exist at the same distance from the two atoms. But diatomic molecules of compounds have some dipole moment and so their structures are asymmetrical.

(c) Triatomic molecules may also be either polar or non-polar. The dipole moment of carbon dioxide is zero. So, it is a non-polar molecule, even though the C—O bonds are polar, as the shared electrons lie closer to the oxygen atom than to the carbon atom. This shows that CO_2 molecule is linear, as only in this way the dipole moment on one side of the molecule is cancelled by that on the other side and the net dipole moment is zero. So, it has the structure $O = C = O$. Similarly, carbon disulphide (CS_2) has a symmetrical linear structure, as its dipole moment is zero. It is non-polar and may be represented as $S = C = S$.

Water on the other hand, has an appreciable dipole moment ($\mu = 1.85D$). Thus, water cannot be linear. The two hydrogen atoms in a water molecule do not lie linearly on the two sides of the oxygen atom like H—O—H. Therefore, it should have an ***unsymmetrical*** or ***bent structure*** as represented by (fig. 8a). The dipole moment of each O—H bond is $1.60D$ and the angle between these two bonds should be 109°6′ to have the dipole moment of the molecules as $1.85D$. (The dipole moment M of the molecule is given by, $\mu = 2m \cos \theta/2$, where m is the bond moment and θ is the angle between the two bonds). The dipole moment for a single H—S bond is nearly $0.8D$ and so the angle between the two bonds in the molecule of H_2S may be found to be 93°. Its structure is represented by figure 8b.

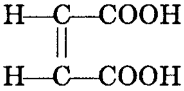
(b) Tetratomic molecules of the type BA_3 may be polar or non-polar. If it is non-polar *e.g.*, BCl_3 then all the atoms will lie in one plane and the angles between the different bonds are equal to one another as shown in figure 8c. The chlorine atoms will be situated at the corners of an equilateral triangle and boron atom will be situated at the point of intersection of the three medians. Ammonia molecule has $\mu = 1.26D$ and its structure is as shown in figure 8d. It is assigned a triangular pyramidal structure in which nitrogen atom lies at the apex of the pyramid and the hydrogen atoms lie at the three corners of the triangle, which forms the base of the pyramid. Molecules of PCl_3 or $AsCl_3$ also have triangular pyramidal structures, with P and As atoms at the apex.



(a) (b) (c) (d)

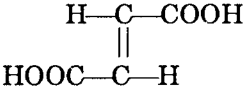
Fig. 8.

(2) In distinguishing between cis and trans isomers : Dipole moment helps us in distinguishing between the cis and trans isomers of a compound. Consider for example, the case of maleic acid and fumaric acid. The cis form will have a dipole moment but in the trans form the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.



$$\begin{array}{l} H—C—COOH \\ \quad\ \| \\ H—C—COOH \end{array}$$

Maleic acid
(cis form)



$$\begin{array}{l} \qquad\quad H—C—COOH \\ \qquad\qquad\ \| \\ HOOC—C—H \end{array}$$

Fumaric acid
(trans form)

(3) In calculating the ionic character of a bond : Dipole moment helps us in determining the ionic character of a covalent bond. It has been seen that the H—Cl bond is 17% ionic in nature.

(4) In determining the polarity of a bond : Dipole moment gives us an indication of the polar character of a bond. The dipole moments of HF, HCl, HBr and HI are 1.92, 1.04, 0.78 and 0.83*D*, respectively. This shows that the polarity of the H—X bond decreases gradually as we move from fluorine to iodine (where, X = F, Cl, Br or I).

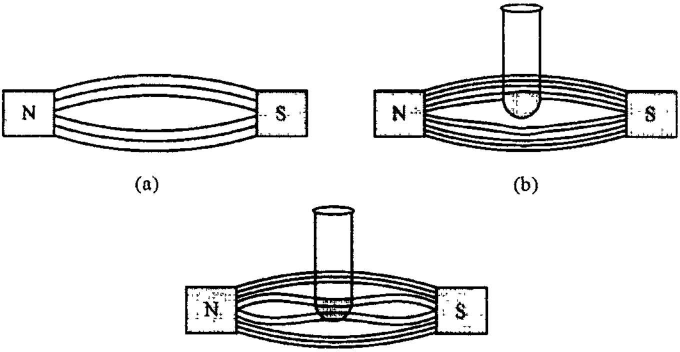
(5) In getting information regarding aromatic substitution : Dipole moments of the ortho, meta and para derivatives of benzene give us valuable information. The angles between the two substituents say nitro are 60°, 120° and 180°, respectively for the three dinitro benzenes. If both the substituents are the same, the dipole moment of para derivative should be zero. Its value will be maximum for the ortho derivative, while the dipole moment for the meta derivative will lie between that of para derivative and ortho derivative.

Problem 6. ***Define the terms:magnetic permeability and magnetic susceptibility of magnetic substances.*** **(Meerut 2006)**

The force F acting between two magnetic dipoles of pole strengths m_1 and m_2 separated by a distance r, is given by

$$F = \frac{1}{\mu} \cdot \frac{m_1 m_2}{r^2} \qquad \ldots (1)$$

where μ is a constant characteristic of the medium and is called ***magnetic permeability*** of the medium. It measures the tendency of the magnetic lines of force to pass through the medium, compared with their tendency to pass through vacuum for which $\mu = 1$. A substance is said to be **diamagnetic** when $\mu < 1$ and **paramagnetic** when $\mu > 1$. So, a diamagnetic substance is less permeable to the magnetic lines of force than a vacuum. The magnetic lines of force deflect towards a paramagnetic substance, whereas they deflect away from a diamagnetic substance.



(a) (b)

(c)

Fig. 9. Magnetic lines of force showing the effect of diamagnetic and paramagnetic substance on the magnetic field.
(a) Vacuum (b) Diamagnetic (c) Paramagnetic.

The magnetic properties of matter are defined in terms of the magnetic field intensity vector, H and the magnetic induction or magnetic flux density, B. When a substance is placed in a magnetic field, the magnetic moment per unit volume, *i.e.*, magnetization, M is related to B and H by the expression,

$$B = \mu_0 (H + M) \qquad \ldots (2)$$

where μ_0 is the permeability of vacuum.

Also, we have

$$B = \mu H \qquad \ldots (3)$$

From equations (2) and (3),

$$M = H\,[(\mu/\mu^0) - 1]$$
$$= H\,(\mu_r - 1) \qquad \ldots (4)$$

where $\mu_r = \frac{\mu}{\mu_0}$ which is known as relative permeability of the medium. ($\mu_0 = 4\pi \times 10^{-7}$ JC^{-2} m^{-1} s^2).

Another term, **magnetic subsceptibility,** is defined as

$$\chi = M/H = \mu_r - 1$$

Magnetic susceptibility is a dimensionless quantity. The **molar magnetic susceptibility,** is defined as

$$\chi_m = V_m \chi$$

where V_m is the molar volume.

Magnetic susceptibility and magnetic permeability are related to each other as

$$\chi = \frac{(\mu - 1)}{4\pi\rho}$$

where ρ is the desnity in g cm^{-3}.

Problem 7. ***Explain the following magnetic properties :***

(i) Paramagnetism and paramagnetic substances

(ii) Diamagnetism and diamagnetic substances

(iii) Ferromagnetism and ferromagnetic substances.

In 1845, Faraday made a very important discovery that magnetism was a property which affected all bodies. In his experimental researches he found that the magnetic properties were not confined to a few elements like iron, nickel, cobalt etc. but that all substances and all forms of matter possess magnetic properties to some degree. He divided all the substances into three different types, *viz., ferromagnetic, paramagnetic and diamagnetic,* according to their behaviour in a magnetic field.

[I] Paramagnetism and Paramagnetic Substances

Those substances which are attracted by magnets and when placed in a magnetic field move from weaker to stronger parts of the field are called paramagnetic substances. This phenomenon is known as paramagnetism.

The susceptibility of a paramagnetic substance has a small positive value and is inversely proportional to the absolute temperature and thus obeys Curie's law. If a paramagnetic substance is kept in a magnetic field, the lines of force tend to accummulate it, as shown in figure (9).

Paramagnetic substances are much larger in number and consist of many metallic elements, some gases and most of the salts and oxides of the elements belonging to different transitional series, *i.e.*, from Sc (21) to Cu (29), from Y (39) to Pd (46) and the rare-earths Ce (58) to Yb (70), and also the elements belonging to the Pt and U-families.

[II] Diamagnetism and Diamagnetic Substances

Those substances which are repelled by magnets and when placed in a magnetic field move from stronger to weaker parts of the field are called diamagnetic substances. This phenomenon is known as diamagnetism.

The magnetic susceptibility of such substances has a small value and the value does not change with temperature. If a diamagnetic substance is kept in a magnetic field, the lines of forces tend to move away from the substance fig. (9). All other substances which are not paramagnetic are diamagnetic, *e.g.*, Zn, Cd, Hg, Sb, Bi etc.

[III] Ferromagnetism and Ferromagnetic Substances

Those substances which are attracted by the magnets and can also be magnetised are called ferromagnetic substances. This phenomenon is known as ferromagnetism.

Ferromagnetic substances are rather few in number and consist of the three elements Fe, Co, Ni; most of their alloys having a sufficient concentration of the metals, some of their compounds, *e.g.*, the oxides and sulphides of iron, the Heussler alloys (composition : Al 70%, Mn 20%, Cu 10% approx); as also some compounds of manganese and some ferrites of the type MeO, Me_2O_3 where Me is a metal of the iron group. Ferromagnetic substances show all the properties of paramagnetic substances to a much greater degree. The susceptibility has a positive value and the permeability is also very large. The susceptibility (IC) decreases as the temperature increases and obeys Curie's law, *i.e.*, $\kappa \alpha \frac{1}{T}$

It is observed that as temperature is increased, the value of susceptibility drops suddenly at a particular temperature, known as ***Curie point*** or ***critical temperature***. At Curie point, the substance becomes paramagnetic. Curie points for cobalt and nickel are 1100°C and 400°C, respectively. It is also seen that above the Curie point, the susceptibility of a ferromagnetic substance is proportional to the difference of temperatures between the material and Curie point. This is known as ***Curie-Weiss law.***

Problem 8. ***How are magnetic substances classified ? Explain properties of these substances.*** **(Meerut 2007)**

See problem 7.

EXERCISE

[I] Short Answer Type Questions

1. Explain optical isomerism by taking suitable examples.
   [For answer, please see problem 1]
2. Explain the phenomenon of optical activity.
   [For answer, please see problem 1]
3. Explain the term polarisability.
   [For answer, please see problem 3]
4. Derive Debye equation.
   [For answer, please see problem 3]
5. What do you understand by electrical polarisation ?
   [For answer, please see problem 3]
6. How dipole moment is used to elucidate the molecular structure ?
   [For answer, please see problem 5]
7. Explain magnetic susceptibility. **(Meerut 2006)**
   [For answer, please see problem 6]
8. Describe the classification of magnetic substances.
   [For answer, please see problem 7]

[II] Very Short Answer Type Questions

1. Define optical activity with one example. **(Meerut 2006)**
   [For answer, please see problem 1]
2. Define the terms, optical rotation and specific rotation.
   [For answer, please see problem 1]
3. Mention the factors affecting uptical rotation.
   [For answer, please see problem 1]
4. Define dipole moment. **(Meerut 2007)**
   [For answer, please see problem 2]
5. Mention the unit of dipole moment.
   [For answer, please see problem 2]
6. Write Clausius-Mosotti equation.
   [For answer, please see problem 3]
7. Define paramagnetism and paramagnetic substances.
   [For answer, please see problem 7]
8. Define diamagnetism and diamagnetic substances.
   [For answer, please see problem 7]
9. What is Curie-Weiss law ?
   [For answer, please see problem 7]

❑❑❑

UNIT-5

SOLUTIONS, DILUTE SOLUTIONS AND COLLIGATIVE PROPERTIES

Ideal and non-ideal solutions, methods of expressing concentrations of solutions, activity and activity coefficient.

Dilute solution, colligative properties, Raoult's law, lowering of vapour pressure, molecular weight determination. Osmosis, laws of osmotic pressure and its measurement, determination of molecular weight from osmotic pressure. Elevation of boiling point and depression of freezing point. Thermodynamic derivation of relation between molecular weight and elevation in boiling point and depression in freezing point. Experimental methods for determining various colligative properties.

Abnormal molar mass, degree of dissociation and association of solutes.

PROBLEMS

Problem 1. ***Describe the various methods of expressing the concentration of a solution.***

The different methods used to express the concentration of a solution are as given below.

(i) Percentage by weight or weight percentage : *The amount of solute in grams present in 100 grams of the solution is known as weight percentage.*

$$\therefore \quad \text{Percentage by weight} = \frac{\text{Weight of the solute}}{\text{Weight of the solution}} \times 100$$

(ii) Strength : *The strength of the solution is defined as the number of grams of the solute dissolved per litre of the solution.*

$$\therefore \quad \text{Strength} = \frac{\text{Weight of the solute in grams}}{\text{Volume of the solution in litres}}$$

(iii) Molarity : *The number of moles of the solute dissolved per litre of the solution is known as its molarity. It is denoted by M.*

$$\therefore \quad \text{Molarity} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in litres}}$$

$$= \frac{\text{Strength of the solution in grams per litre}}{\text{Mol. wt. of the solute}}$$

For example, 0.1M HCl means a solution containing 0.1 mole (or 3.65 g) per litre of solution.

(iv) Molality : The number of moles of solute present in 1000 grams (or 1 kilogram) of solvent is known as the molality of solution. It is denoted by *m*.

$$\therefore \quad \text{Molality} = \frac{\text{Number of moles of the solute}}{\text{Weight of the solvent in grams}} \times 1000$$

$$= \frac{\text{Number of grams of the solute per 1000 g of the solvent}}{\text{Mol. wt. of the solute}}$$

For example, 0.1 molal solution means a solution containing 0.1 mol of the solute dissolved per 1000 g of the solvent and is written as 0.1 m.

(v) Normality : *The number of gram equivalents of the solute dissolved per litre of the solution is known as its normality.* It is denoted by N.

$$\therefore \quad \text{Normality} = \frac{\text{Number of gram equivalents of the solute}}{\text{Volume of the solution in litres}}$$

$$= \frac{\text{Strength of the solution in grams per litre}}{\text{Equivalent wt. of the solute}}$$

For example, 1N NaCl solution means a solution containing one gram equivalent (*i.e.* 58.5 g) of NaCl dissolved per litre of the solution. It is read as one normal.

(vi) Mole fraction : *The mole fraction of a component in a solution is defined as the number of moles of that component divided by the total number of moles of all the components.*

Mole fraction of the solute in the solution (x_1)

$$= \frac{\text{No. of moles of the solute}}{\text{No. of moles of solute + No. of moles of solvent}}$$

Mole fraction of solvent in the solution (x_2)

$$= \frac{\text{No. of moles of the solvent}}{\text{No. of moles of solute + No. of moles of solvent}}$$

For example if n_1 moles of the solute are dissolved in n_2 moles of the solvent, we may write

$$x_1 = \frac{n_1}{n_1 + n_2} \text{ and } x_2 = \frac{n_2}{n_1 + n_2}$$

$$\therefore \quad x_1 + x_2 = \frac{n_1}{n_1 + n_2} + \frac{n_2}{n_1 + n_2} = \frac{n_1 + n_2}{n_1 + n_2} = 1.$$

NUMERICAL PROBLEMS

Ex. 1. ***Calculate the molarity of a solution of sodium chloride (Na = 23 and Cl = 35.5) which contains 60 g of sodium chloride in 2000 ml of solution.***

Sol. 2000 ml = 2 litre.

$$\text{No. of moles of sodium chloride} = \frac{60}{23 + 35.5} = \frac{60}{58.5}$$

$$2 \text{ litre of the solution contains} = \frac{60}{58.5} \text{ moles of the solute}$$

$$1 \text{ litre of the solution contains} = \frac{60}{58.5} \times \frac{1}{2} = \frac{30}{58.5}$$

$$= 0.513 \text{ moles}$$

∴ Molarity of the solution = **0.513 M**

Ex. 2. ***0.212 g of Na_2CO_3 with molecular mass 106 is dissolved in 250 ml of the solution. Calculate the molarity of Na_2CO_3 in the solution.***

Sol. No. of moles of $Na_2CO_3 = \frac{0.212}{106}$ moles

250 ml of the solution contains $= \frac{0.212}{106}$ moles

1000 ml of the solution conains $= \frac{0.212 \times 1000}{106 \times 250}$ moles

$= 0.008$ moles

Hence, molarity of the solution = **0.008 M**

Ex. 3. ***Find the molarity and molality of a 15% solution of H_2SO_4 (density of H_2SO_4 = 1.10 g/ml and molecular mass of H_2SO_4 = 98).***

Sol. (i) Molarity

100 ml of the solution contains = 15 g H_2SO_4

1000 ml of the solution contains $= \frac{15}{100} \times 1000$ g H_2SO_4

$= 150$ g H_2SO_4

or $= \frac{150}{98}$ moles or 1.53 moles

∴ Molarity of the solution = **1.53 M**

(ii) Molality

Mass of 100 ml of solution= 1000×1.10 (volume × density)

= 1100 g

Mass of the acid = 150 g

Mass of water = (1100 − 150) g

= 950 g

950 g water contains = 1.53 moles of H_2SO_4

1000 g water contains $= \frac{1.53}{950} \times 1000 = 1.61$ moles

∴ Molality of the solution = **1.61 m**

Ex. 4. ***Calculate the mole fraction of water in a mixture of 12 g of water, 108 g of acetic acid and 92 g of ethyl alcohol.***

Sol. Mass of water $= 12$ g

Mol. mass of water $= 18$

No. of moles of H_2O (n_1) $= \frac{12}{18} = 0.66$

Mass of acetic acid $= 108$ g

Mol. mass of acetic acid $= 60$

No. of moles of acetic acid $(n_2) = \frac{108}{60} = 1.8$

Mass of ethyl alcohol $= 92$ g

Mol. mass of ethyl alcohol $= 46$

No. of moles of ethyl alcohol (n_3) $= \frac{92}{46} = 2$

Total no. of moles, $n_1 + n_2 + n_3 = 0.66 + 1.8 + 2$

Mole fraction of water, $x_1 = \frac{n_1}{n_1 + n_2 + n_3}$

$= \frac{0.66}{0.66 + 1.8 + 2} = \mathbf{0.148}$

Ex. 5. ***A solution contains 25% ethanol, 50% acetic acid and 25% water by mass. Calculate the mole fraction of each component.***

Sol. Let the total mass of the solution be 100 g.

(i) Mass of ethanol $= 25$ g

No. of moles of ethanol $= \frac{25}{46} = 0.544$

(ii) Mass of acetic acid $= 50$ g

No. of moles of acetic acid $= \frac{50}{60} = 0.833$

(iii) Mass of water $= 25$ g

No. of moles of water $= \frac{25}{18} = 1.39$

Total no. of moles of the three components

$= 0.544 + 0.833 + 1.39$

$= 2.767$

Mole fraction of ethanol $= \frac{0.544}{2.767} = \mathbf{0.196}$

Mole fraction of acetic acid $= \frac{0.833}{0.767} = \mathbf{0.302}$

Mole fraction of water $= \frac{1.39}{2.797} = \mathbf{0.502}$

Ex. 6. ***Calculate mole fraction of glucose in solution of 9 gm glucose in 180 gm water.*** **(Meerut 2007)**

Sol. No. of moles of glucose $= \frac{9}{180} = \frac{1}{20} = 0.05$

No. of moles of water $= \frac{180}{18} = 10$

Total number of moles in solution

$= 0.05 + 10 = 10.05$

$\therefore$ Mole fraction of glucose $= \frac{0.05}{10.05} = \mathbf{0.0049}$

Ex. 7. ***2.82 g of glucose (mol. mass =180) are dissolved in 30 g of water. Calculate :***

(i) Molality of the solution

(ii) Mole fractions of (a) glucose and (b) water.

Sol. (i) 30 g H_2O contains = 2.82 g of glucose

1000 g H_2O contains $= \frac{2.82}{30} \times 1000$ g of glucose

$= \frac{2.82 \times 1000}{30 \times 180}$ moles of glucose

$= 0.52$ moles

$\therefore$ Molality of the solution $= \mathbf{0.52\ m}$

(ii) No. of moles of glucose, $n_1 = \frac{2.82}{180}$

No. of moles of water, $n_2 = \frac{30}{18}$

Mole fraction of glucose, $x_1 = \frac{2.82/180}{2.82/180 + 30/18} = \mathbf{0.0093}$

As $x_1 + x_2 = 1$

$\therefore$ $x_2 = 1 - x_1$

$\therefore$ Mole fraction of water $x_2 = 1 - 0.0093$

$= \mathbf{0.9907}$

Ex. 8. ***4.0 g of NaOH is contained in a deci-litre of a solution (density = 1.038 g/mol). Calculate the following :***

(i) Mole fraction of NaOH

(ii) Molarity of NaOH

(iii) Molality of NaOH

Sol. (i) Mole fraction of NaOH

Volume of the solution = 100 ml, Density = 1.038 g/ml

Mass of 100 ml of the solution = 1.038 × 100 = 103.8 g

Mass of NaOH = 4.0 g

∴ Mass of water = (103.8 – 4) g = 99.8 g

No. of moles of NaOH $= \frac{4}{40} = 0.1$

No. of moles of water $= \frac{99.8}{18} = 5.54$

∴ Mole fraction of NaOH $= \frac{0.1}{0.1 + 5.54} = \frac{0.1}{5.64}$

$= \mathbf{0.018}$

(ii) Molarity of NaOH

100 ml of the solution contains = 0.1 mole of NaOH

1000 ml of the solution contains $= \frac{0.1 \times 1000}{100}$ mole of NaOH

= 1 mole of NaOH

∴ Molarity of the solution = **1*M***

(iii) Molality of NaOH

99.8 g water contains = 0.1 mole of NaOH

1000 g water contains $= \frac{0.1}{99.8} \times 1000$ moles of NaOH

= 1.002 moles

Hence, molality of the solution = **1.002 m**

Problem 2. ***What are ideal and non-ideal solutions ? Mention their characteristics.***

[I] Ideal Solutions

A solution of two components is said to be ideal if each component of the solution obeys Raoult's law at all temperatures and concentrations, *i.e.*, the vapour pressure of each component in the solution at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state at the same temperature. So, if two liquids A and B are mixed together, the solution formed by them will be ideal, if

$$p_A = x_A \times p_A^0$$

and $$p_B = x_B \times p_B^0$$

where p_A = vapour pressure of component A in the solution

x_A = mole fraction of the component A in the solution

p_A^0 = vapour pressure of the liquid A in the pure state

and p_B, x_B, p_B^0 are the corresponding terms for the component B.

It is seen that *the solution formed by two liquids* A *and* B *is ideal if the interactions (i.e., the intermolecular forces of attraction) among the molecules of* A *and* B *in the solution are just the same as among the molecules of pure* A or B.

Further, it can also be observed that the solution formed on mixing the two liquids is ideal, if

(i) There is no volume change on mixing, i.e., $\Delta V_{\text{mix}} = 0$

(ii) There is no enthalpy change on mixing, i.e., $\Delta H_{\text{mix}} = 0$

For example, if 100 ml of *n*-hexane are mixed with 100 ml of *n*-heptane, the total volume of the solution is found to be 200 ml and the temperature of the solution is found to be the same as that of pure *n*-hexane and *n*-heptane before mixing showing that no heat is evolved or absorbed on mixing. Such a solution is an ideal solution.

[II] Non-Ideal or Real Solutions

A solution formed by mixing two liquids is said to be non-ideal, if it does not obey Raoult's law or the interactions of A and B molecules in the solution are not similar to those of pure A and pure B. Furthermore, $\Delta V_{\text{mix}} \neq 0$ and $\Delta V_{\text{mix}} \neq 0$.

Problem 3. *Draw vapour pressure-composition diagram for ideal solutions.*

In case of ideal solutions, the partial pressure of each component can be calculated using Raoult's law, *i.e.*,

$$p_A = x_A \times p_A^0$$

and $$p_B = x_B \times p_B^0$$

where, p_A, p_A^0, p_B and p_B^0 are all measured at the same temperature. Thus, the total prossure of the solution (P) is given by,

$$P = x_A\, p_A^0 + x_B\, p_B^0$$

At any particular temperature, the values of P can be determined experimentally for different mole fractions. The values

p_A^0 and p_B^0 for the pure liquids can be measured at the same temperature and hence p_A and p_B can be calculated for any particular mole fraction. For an ideal solution, straight lines are obtained for curves between vapour pressures and composition as shown in figure (1). The dotted lines represent the curves of the partial pressures and the solid line represents the curve of the solution.

In these plots, for any mole fraction (say x), the total vapour pressure of the solution is the sum of the partial pressures of its components A and B.

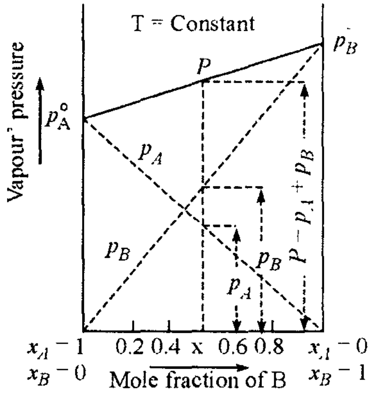


Fig. 1. Vapour pressure-composition diagram for an ideal solution.

Problem 4. *Draw vapour pressure-composition curves for non-ideal solutions.*

In case of non-ideal solutions, the plots between vapour pressure and composition (mole fraction) are curved lines instead of straight lines. Non-ideal solutions show the following three types of deviations from Raoult's law.

Type I : ***Those which show small positive deviation from Raoult's law.*** The vapour pressure-composition graph of these solutions are slightly upwards as shown in figure (2). The dotted straight line plots are for ideal solution, calculated by using Raoult's law. The full lines show curves for non-ideal or real solutions.

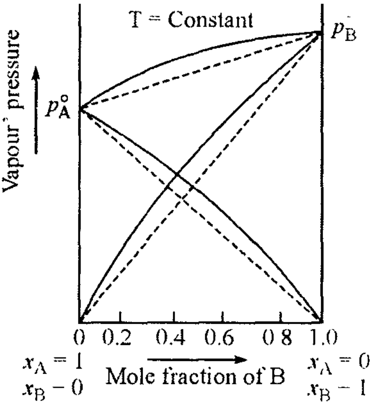


Fig. 2. Vapour pressure-composition plots for non-ideal solution showing small positive deviation.

Examples : Benzene + toluene, water + methyl alcohol, carbon tetrachloride + cyclohexane etc.

Type II : ***Those which show large positive deviation from Raoult's law.*** The vapour pressure-composition plots of these solutions are appreciably upwards as shown in figure (3). The dotted straight line plots, included in the figure for comparison, are for ideal solutions (calculated by means of Raoult's law). The full lines show curves for non-ideal or real solutions.

It is thus clear from figs. (2) and (3) that for any mole fraction, the total vapour pressure of the solution is more than that for ideal solution. This means that the tendency for the molecules to escape from the solution is more than from the pure liquids. This shows that in such solutions, the intermolecular forces of attraction between the molecules of the solution (A-B attractions) are weaker than those of either of the pure components (A-A attractions or B-B attractions). Such a behaviour is associated with an increase in volume and absorption of heat on mixing.

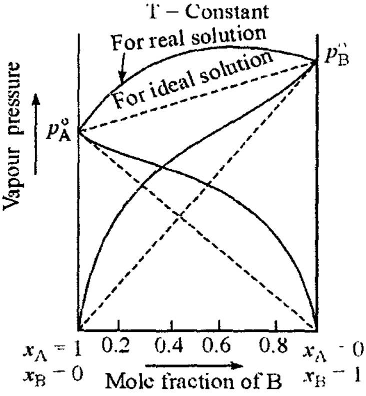


Fig. 3. Vapour pressure-composition plots for non-ideal solution showing large positive deviation.

Examples : Water + ethanol, ethanol + chloroform etc.

Type III : ***Those which show negative deviation from Raoult's law.*** The vapour pressure-composition plots of these solutions are downwards as shown in figure (4). The dotted straight line plots are for the ideal solution, calculated on the basis of Raoult's law and are included in the figure for comparison. (The full lines show curves for non-ideal or real solutions). It is clear from the figure that for any mole fraction, the total vapour pressure of the solution is less than that for ideal solution. This means that the tendency for the molecules to escape from the solution is less than that from the pure liquids. This shows that in such solutions, the intermolecular forces of attraction between the molecules of the solution (A-B attractions) are stronger than those of either of the pure components (A-A attractions or B-B attractions). It is related to the contraction in volume and evolution of heat in making the solution.

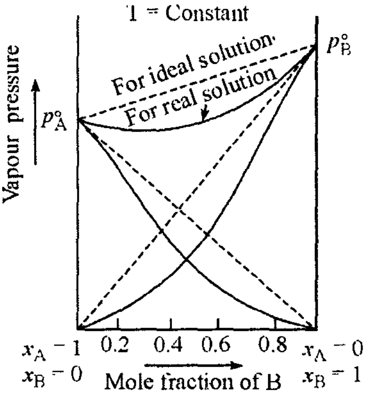


Fig. 4. Vapour pressure-composition plots for non-ideal solution showing negative deviation.

Examples : Water + nitric acid, water + sulphuric acid, acetone + chloroform etc.

Problem 5. ***Explain the following terms :***

(i) Activity,

(ii) Activity coefficient,

(iii) Mean activity of ions, and

(iv) Mean activity coefficient of ions.

[I] Activity

Guldberg and Waage (1867) enunciated the law of mass action which states that, *'the rate of a reaction is proportional to the product of the active masses of the reactants'*. In case of gases, partial pressures can be used in place of active masses as the two are proportional to each other. But when substances react in solution, it does not necessarily follow that their concentrations correspond entirely to their active masses. This would occur only if the solutions are ideal, *i.e.*, for dilute solutions. Suppose for example, one component becomes hydrated or solvated; and if only the non-solvated portion can react then it is only this portion that contributes to the active mass.

Ideal and Non-Ideal Gases. It has been experimentally observed that at very low densities, all gases obey the expression $PV = nRT$, irrespective of the chemical composition of gases. That gas for which the above relation remains the same under all conditions is known as an **ideal** or **perfect gas**. For an ideal gas, the volume of the molecule can be neglected in comparison to the total volume of the gas, and the molecular attraction between the molecules is negligible. But deviations are observed as the above conditions are not always fulfilled. Then an ideal gas becomes a real or non-ideal gas. In other words, the behaviour of a real gas approaches the ideal gas as the pressure aproaches zero.

$$\therefore \quad \underset{P \to 0}{\text{Lt}} \text{ Real gas} \to \text{Ideal gas}$$

If the total concentration be c and that of the non-solvated molecules be a, then the ratio a/c is known as ***active fraction***. The effective concentration or the concentration of the non-solvated molecules is known as ***activity***. This concept was given by G.N. Lewis (1908).

[II] Activity Coefficient

The term a/c is termed as *activity coefficient* and is usually represented by f of γ. So,

$$\frac{a}{c} = f \text{ or } \gamma \qquad \dots (1)$$

The same idea, has been applied to solutions of strong electrolytes. In the case of an ideal solution, the value of f or γ is unity.

Consider the following reaction to take place in solution :

$$A + B \rightleftharpoons C + D$$

The equilibrium constant will be given by,

$$K = \frac{a_C \times a_D}{a_A \times a_B}$$

where, a_A, a_B, a_C and a_D represent the ideal concentrations or activities of the respective constituents A, B, C and D. The concentration can also be expressed in terms of molality (m) which is defined as, *"number of moles of solute present in 1000 gram of the solvent".*

The ratio a/m is also known as **activity coefficient** (f). The activity coefficient may, therefore, be regarded as the measure of extent to which an ion or molecule departs from the ideal behaviour, since 'a' represents the ideal concentration and 'c' or 'm' the real concentration.

[III] Mean Activity of Ions

Consider a uni-univalent electrolyte of type BA, (*e.g.*, NaCl, KCl etc) whose ionisation can be considered as follows :

$$BA \rightleftharpoons B^+ + A^-$$

The equilibrium constant (k) will then be given by,

$$k = \frac{[B^+]\,[A^-]}{[BA]} = \frac{a_+\, a_-}{a_2} \qquad \ldots (2)$$

where a_+ is activity of the cation (B^+), a_-, is activity of the anion (A^-), a_2 is activity of the undissociated electrolyte (BA).

The *mean activity of the two ions* ($a_\pm$) may be regarded as the geometric mean of the activities of the respective ions.

$$\therefore \qquad a_\pm = \sqrt{(a_+ \,.\, a_-)} = (ka_2)^{1/2} \qquad \text{[From eq. (2)]} \qquad \ldots (3)$$

[IV] Mean Activity Coefficient of Ions

The separate activity coefficients of the ions are,

$$f_+ = a_+\, c_+ \text{ and } f_- = a_- /c_-$$

The mean activity coefficient ($f_\pm$) of the two ions is regarded as the geometric mean of the activity coefficients of the ions. So,

$$f = f_\pm = \sqrt{(f_+\, f_-)}$$

$$= \sqrt{\left(\frac{a_+}{c_+} \cdot \frac{a_-}{c_-}\right)} = \frac{a_\pm}{c_\pm}$$

$$= \frac{(ka_2)^{1/2}}{c} \quad \text{[From equation (3)]}$$

where $c_{\pm} = c$.

In general, for an electrolyte which dissociates into ν_+ cations and ν_- anions, we have,

$$B_{\nu+}\, A_{\nu-} \rightleftharpoons \nu_+\, B^+ + \nu_-\, A^-$$

Let a_+, a_- and a_2 be the activities of the cations, anions and undissociated electrolyte, respectively, then,

$$ka_2 = a_+^{\nu_+}\, a_-^{\nu-}$$

The mean activity is then given by,

$$a_{\pm} = (a_+^{\nu_+}\, a_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$$

$$= (a_+^{\nu_+}\ a_-^{\nu_-})^{1/\nu} = (ka_2)^{1/\nu} \qquad \dots (4)$$

where $\nu =$ total number of ions $= \nu_+ + \nu_-$

If the total concentration of the electrolyte is c, then the activity coefficients of the ions* are :

$$f_+ = \frac{a_+}{\nu_+\, c} \quad \text{and} \quad f_- = \frac{a_-}{\nu_-\, c} \qquad \dots (5)$$

The mean activity coefficient of the electrolye is given by,

$$f_{\pm} = (f_+^{\nu_+} \,.\, f_-^{\nu_-})^{1/\nu}$$

$$= \left[\left(\frac{a_+}{\nu_+\, c}\right)^{\nu_+}\left(\frac{a_-}{\nu_-\, c}\right)^{\nu_-}\right]^{1/\nu} \quad \text{[From eq. (5)]}$$

$$= (a_+^{\nu+} \,.\, a_-^{\nu-})^{1/\nu}/[(\nu_+\, c)^{\nu+} \,.\, (\nu_-\, c)^{\nu-}]^{1/\nu}$$

$$= \frac{a_{\pm}}{c_{\pm}} \qquad \dots (6)$$

where $c_{\pm} = [(\nu_+\, c)^{\nu+} \,.\, (\nu_-\, c)^{\nu-}]^{1/\nu} = c\, (\nu_+^{\nu+} \,.\, \nu_-^{\nu-})^{1/\nu}$ ... (7)

The factor $[\nu_+^{\nu-} \,.\, \nu_-^{\nu-}]^{1/\nu}$ is known as ***'valency factor.'***

From equations (4), (6), (7) we get,

$$f_{\pm} = (ka_2)^{1/\nu} c_{\pm} \qquad \dots (8)$$

Note. If molality (m) is used in place of concentration (c), then in all the above expressions, c can be replaced by m.

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* For KCl : $f_{Cl^-} = \frac{a_-}{c}$; for BaCl$_2$: $f_{Cl^-} = \frac{a_-}{2c}$· for FeCl$_3$: $f_{Cl^-} = \frac{a_-}{3c}$

Problem 6. ***What is meant by osmosis and discuss its mechanism? How does it differ from diffusion?***

[I] Osmosis

Consider a solution of sugar contained in an inverted thistle funnel, the lower end of which is tied with a parchment paper, which acts as semi-permeable membrane. This funnel is then kept in a beaker containing water, as shown in figure (5). Water passes into the funnel through the membrane, whereby the level of the liquid in the funnel is risen appreciably. *The phenomenon of spontaneous flow of pure solvent (water) into a solution through a semi-permeable membrane is known as osmosis.*

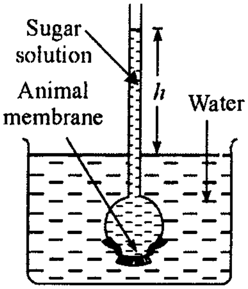

Fig. 5. Osmosis

Osmosis not only occurs between a pure solvent and a solution but also between two solutions of different concentrations.

So, **osmosis** may also be defined as, *'the spontaneous flow of solvent through a semi-permeable membrane from a solution of lower concentration to that of higher concentration'.* If two solutions are of equal concentrations, no osmosis will take place*.

[II] Mechanism of Osmosis

In order to explain the mechanism of osmosis, it has been assumed that the solvent simply passes from a region in which it has a greater tendency to escape to a region in which it has a lower escaping tendency. Moreover, it has also been assumed that the solvent moves due to its attraction for a solute, a phenomenon known as *solvent action.*

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* The following experiment demonstrates the phenomenon of osmosis.

Suppose the outer hard shell of two eggs of the same size is removed by dissolving in dil. HCl. One egg is placed in distilled water and the other in saturated salt solution. After some hours, it will be seen that the egg placed in water swells and the one placed in salt solution shrinks. In the former, water diffuses through the skin (s.p.m) into the egg material which swells. In the latter case, the concentration of the salt solution is higher than the egg material, so the egg shrinks.

[III] Difference Between Diffusion and Osmosis

S.No.	Diffusion	Osmosis
1.	The process of diffusion of the solute in a solvent is due to (i) motion of solute molecules from a concentrated solution into the solvent and (ii) motion of solvent molecules into the concentrated solution.	The process of osmosis is due to the passage of solvent through a semi-permeable membrane from a solution of lower concentration to that of higher concentration.
2.	Presence of semi-permeable membrane is not essential.	Presence of semi-permeable membrane is essential.
3.	Both solute as well as solvent molecules flow in opposite directions.	Only solvent molecules flow.

Problem 7. ***(a) Define osmotic pressure.***

(b) Describe important methods for determining the osmotic pressure of solution. What is the effect of temperature and concentration on the osmotic pressure of a dilute solution?

(c) How is osmotic pressure of a solute in a non-aqueous solvent determined?

(d) How is osmotic pressure used for finding out the molecular weight and degree of dissociation of an electrolyte?

(a) Osmotic Pressure

Consider a solution of sugar contained in an inverted thistle funnel, the lower end of which is tied by a parchment paper, which acts as a semi-permeable membrane. This funnel is then kept in a beaker containing water as shown in figure (6). Water passes into the funnel through the membrane, whereby the level of the liquid in the funnel rises appreciably.

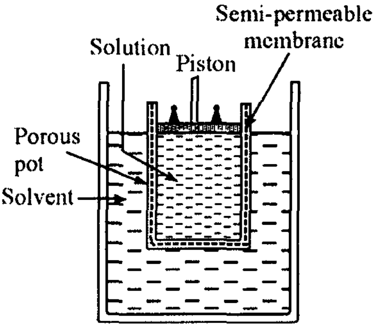

Fig. 6. Balancing of osmotic pressure.

The flow of solvent through the membrane will continue till an equilibrium is established. At this stage, the hydrostatic pressure of the liquid column exactly balances the tendency of water to pass inside through the semi-permeable membrane. ***The hydrostatic pressure thus set up as a result of osmosis is a measure of osmotic pressure of the solution.*** If the liquid rises to a height h in the tube of the funnel, then :

Osmotic pressure of solution = hdg,

where, d is the density of the solution and g is the acceleration due to gravity.

Osmotic pressure can also be defined as follows :

(i) Let the sugar solution be placed in a vessel, the walls of which are semi-permeable. It is tightly closed by a piston. This vessel is lowered into a larger vessel (*e.g.*, beaker) containing pure solvent (water), as shown in figure (6). The water on account of osmosis will have a tendency to flow into the smaller vessel through the semi-permeable membrane. This tendency can be checked by applying external pressure on the solution by placing increasing weights on the piston. By placing proper weights on the piston, the tendency of water to enter the smaller vessel through the membrane will be exactly balanced by its counter pressure from above.

So, **osmotic pressure** of a solution is defined as, ***'the excess pressure which must be applied to the solution in order to just prevent the flow of the solvent into it through a semi-permeable membrane'.***

(ii) In osmosis, the vapours of solvent permeate through a semi-permeable membrane in order to make the vapour pressures the same on both sides. As the vapour pressure of a liquid can be increased by applying pressure on it, osmosis may thus be stopped by applying some extra pressure on the solution or applying some negative pressure on the solvent. The vapour pressures on the two sides are thus equalised. So, ***osmotic pressure*** may be defined as, ***'the excess pressure which must be applied to the solution in order to increase its vapour pressure until it becomes equal to that of the solvent.'***

Alternately, ***osmotic pressure*** is also defined as, ***'the pressure withdrawn externally from the pure solvent in order to decrease its vapour pressure until it becomes equal to that of the solution.'***

(b) Measurement of Osmotic Pressure

Though a number of methods, *e.g.*, Pfeffer's method, de Vries plasmolytic method etc. are available for measuring the osmotic pressure of a solution, the methods mostly used for the purpose are due to (i) Morse and Frazer and (ii) Berkeley and Hartley. These are described below :

(i) Morse-Frazer's method : The apparatus used is as shown in figure (7). The semi-permeable membrane was deposited on the walls of a previously cleaned porous pot. In order to avoid the membrane bursts, the porous pot was set in an inverted position and then filled with pure solvent. The solution was taken in a bronze cylinder, into which the porous pot was fixed. The cylinder was fitted with a manometer. The glass tube fitted into the porous pot and open at both ends served to keep the pot full with solvent at atmospheric pressure.

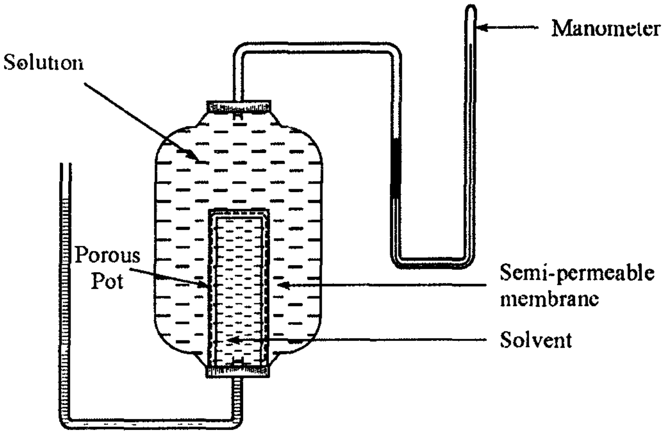

Fig. 7. Morse-Frazer's apparatus.

Due to osmosis, the solvent tended to pass from the porous pot into the cylinder through the semi-permeable membrane. Thus, an excess pressure was developed which was recorded on the manometer.

(ii) Berkeley-Hartley's method : The apparatus (Fig. 8) consists of a porous pot on the walls of which is deposited a semi-permeable membrane of copper ferrocyanide. It is surrounded by a bronze cylinder to which is fitted a piston, P. A pressure gauge is also attached to the piston to measure the osmotic pressure. The porous pot is fitted with a water reservoir on the right side and a capillary A on the left side. Water is placed in the porous pot, while the cylinder is filled with the solution whose osmotic pressure is to be determined. Water tends to pass from the porous pot into the solution through the semi-permeable membrane. This results in the lowering of the level of water in capillary A. Pressure is now applied externally by the piston so that the level of water in the

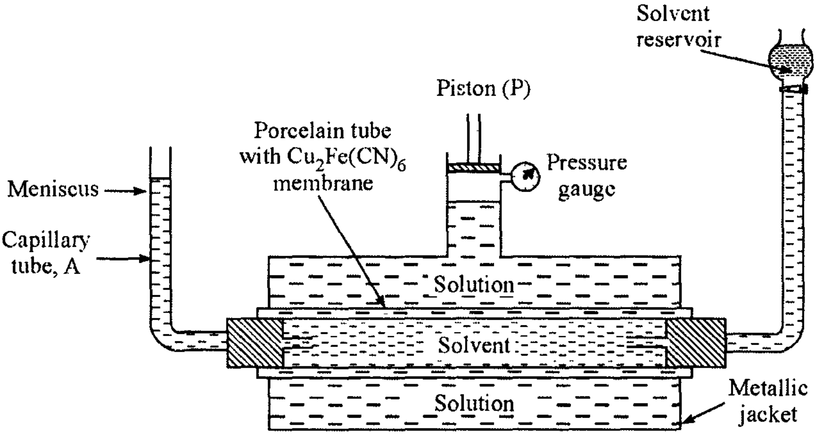

Fig. 8. Berkeley-Hartley's apparatus

capillary A remains stationary. The total applied pressure which is equal to the osmotic pressure of the solution can be read from the pressure gauge or by a manometer.

This method is an improved one in the sense that the equilibrium is established very quickly, strain on the membrane is not so much as in other methods and the concentration of the solution does not change during the measurements.

[I] Effect of Temperature and Concentration on Osmotic Pressure

According to van't Hoff, osmotic pressure of a solution is due to the bombardment of solute particles on semi-permeable membrane. It will thus increase with the increase in the number of solute particles, *i.e.*, concentration of solution. Thus, osmotic pressure is directly proportional to concentration.

Furthermore, the bombardment of the solute particles on semi-permeable membrane depends upon their velocity and the latter in turn increases with temperature. Thus, osmotic pressure increases with increasing temperature, *i.e.*, they are directly proportional to each other.

(c) Measurement of Osmotic Pressure in Non-Aqueous Solvents or Townend's Negative Pressure Method

The special part of this apparatus as shown in fig. (9), is the porous disc. It is made from a special mixture of clay and glass powder. The size of the pores is very small such that only the vapours can pass through it. The air in the bulb is evacuated by a suction pump.

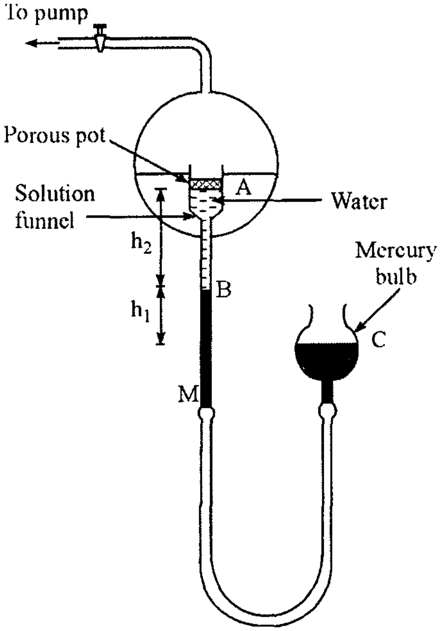

Fig. 9. Townend's porous disc apparatus.

Due to osmosis, the mercury-solvent boundary B, moves up due to escape of vapours from the solvent side. Now the reservoir is moved up and down till the position B remains stationary. The steady level of B confirms that the vapour pressure of solvent has been reduced just sufficiently to become equal to the pressure of the solution. The osmotic pressure (P) of the solution is given by,

$$P = \text{BC} + \frac{\text{AB} \times d}{13.6}$$

or

$$P = h_1 + \frac{h_2 \times d}{13.6} \qquad \text{... (1)}$$

where, d is the density of the solvent, 13.6 g cm^{-3} is the density of mercury.

Advantages :

(i) This method does not require the membranes which are prepared with difficulty.

(ii) This method is particularly useful for solutions in non-aqueous solvents for which suitable membranes are not available.

(d) Molecular Weight From Osmotic Pressure

According to van't Hoff, we have $PV = nRT$
where, $P =$ osmotic pressure; $V =$ volume of the solution, $n =$ number of moles of solute; $R =$ gas constant; $T =$ absolute temperature.

If w g of solute of molecular weight m be dissolved in the solution, then we have $n = w/m$

$$\therefore \qquad PV = \frac{w}{m} RT$$

Thus, the value of m can be calculated, provided the values of P, V, w and T are known.

[I] Calculation of Degree of Dissociation from Osmotic Pressure

Degree of dissociation of solute is defined *as the fraction of the total solute dissociated into ions in solution.*

Let α be the degree of dissociation of NaCl in solution. If we start with one mole of NaCl, then the number of moles of NaCl, Na^+ and Cl^- after dissociation will be as follows :

$$\begin{array}{lccl} NaCl \rightleftharpoons & Na^+ & + \; Cl^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & 0 & 0 & \text{(After dissociation)} \end{array}$$

$\therefore$ Number of particles before dissociation = 1

Number of particles after dissociation $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

As osmotic pressure $\propto$ Normal number of particles in solution

$\therefore$ Normal osmotic pressure $\propto$ Normal number of particles $\propto 1$

Observed osmotic pressure $\propto$ No. of particles after dissociation

$$\propto 1 + \alpha$$

$$\therefore \quad \frac{\text{Normal osmotic pressure}}{\text{Observed osmotic pressure}} = \frac{\text{Number of particles before dissociation}}{\text{Number of particles after dissociation}}$$

Thus, measuring the observed osmotic pressure of the solution by any known method and calculating the normal osmotic pressure (assuming no dissociation of the solute), we can calculate the value of α, degree of dissociation of the solute.

NUMERICAL PROBLEMS

Ex. 1. ***Calculate the osmotic pressure of 5% solution of glucose*** **(*$C_6H_{12}O_6$*)** ***at 18°C.***

Sol. $T = (273 + 18) = 291$ K; $w = 5$.

$V = 100$ c.c. $= 1/10$ litre,

m of glucose $(C_6H_{12}O_6) = 180$.

We know that, $P = \frac{w}{mV} \times RT$

or $P = \frac{5}{180 \times 1/10} \times 0.0821 \times 291 = \mathbf{6.636\ atm.}$

Ex. 2. ***Calculate the osmotic pressure of a solution containing 6 g of urea and 9 g of glucose in one litre solution at 27°C.***

Sol. The O.P. (P_1) of solution due to urea

$$= \frac{w}{mV} . RT = \frac{6 \times 0.0821 \times 300}{60 \times 1} = 2.463 \text{ atm.}$$

The O.P. (P_2) of solution due to glucose

$$= \frac{w}{mV} . RT = \frac{9 \times 0.0821 \times 300}{180 \times 1} = 1.231 \text{ atm.}$$

$\therefore$ Osmotic pressure of the solution

$$= P_1 + P_2 = 2.463 + 1.231 = \mathbf{3.694\ atm.}$$

Ex. 3. ***Calculate the osmotic pressure of 5% urea solution at 0°C.***

Sol. Mol. wt. of urea (NH_2CONH_2)

$$= 14 + 2 + 12 + 16 + 14 + 2 = 60$$

From the equation,

$$P = \frac{w}{mV} . RT$$

we have, $P = \frac{5 \times 0.0821 \times 273}{60 \times 0.1}$ $(\because\ V = 0.1 \text{ litre})$

$$= \mathbf{18.67\ atmosphere.}$$

Ex. 4. ***Calculate the osmotic pressure of M/10 solution of cane sugar at 27°C.***

Sol. Molecular weight of cane sugar ($C_{12}H_{22}O_{11}$) = 342.

For *M*/10 solution, it means that 1/10 g mole of cane sugar is dissolved in 1 litre of solution, *i.e.*, 342/10 g is dissolved in 1 litre.

$$\therefore \quad w = \frac{342}{10} = 34.2 \text{ g}$$

$V = 1$ litre; $T = 27 + 273 = 300$ K; $m = 342$.

We know that,

$$P = \frac{w}{mV} . RT$$

$$= \frac{34.2 \times 0.0821 \times 300}{342 \times 1}$$

$$= \mathbf{2.463 \text{ atmosphere.}}$$

Ex. 5. ***Calculate the osmotic pressure of 0.01 N solution of cane sugar at 27°C (R = 0.0821 litre atmosphere deg^{-1} $mole^{-1}$)***

Sol. We know that,

$$P = \frac{w}{mV} . RT$$

0.01 N solution of cane sugar (mol. wt. = 342) means 0.01 × 342 g, *i.e.*, 3.42 g of it is dissolved in one litre of solution. So,

w = 3.42 g, V = 1 litre, m = 342, T = 300 K

$$\therefore \quad P = \frac{3.42 \times 0.0821 \times 300}{342 \times 1}$$

$$= \mathbf{0.2463 \text{ atmosphere.}}$$

Ex. 6. ***Calculate the osmotic pressure of 10% cane sugar solution at 25°C. (Molecular weight of cane sugar = 342)***

Sol. P = ?, V = 100 ml = 0.1 litre, w = 10 g,

T = 25 + 273 = 298 K, m = 342

We know that, $P = \frac{w}{mV} . RT$

$$\therefore \quad P = \frac{10 \times 0.0821 \times 298}{342 \times 0.1}$$

$$= \mathbf{7.153 \text{ atmosphere.}}$$

Ex. 7. ***Calculate the osmotic pressure of the mixture solution after mixing the following at 20°C :***

(a) 100 ml of 3.4% urea solution (mol. wt. = 60).

(b) 100 ml of 1.5% sugar solution (mol. wt. = 342).

Sol. On mixing, the total volume of the mixture becomes 200 ml.

(a) Osmotic pressure (P_1) of urea solution

$$P = \frac{w}{mV} . RT$$

$$= \frac{3.4 \times 0.0821}{60 \times 0.2}$$

$$= 6.81 \text{ atmosphere}$$

(b) Osmotic pressure (P_2) of sugar solution

$$P = \frac{w}{mV} \cdot RT$$

$$= \frac{1.5 \times 0.0821 \times 293}{342 \times 0.2} = 0.527 \text{ atmosphere}$$

∴ Osmotic pressure of the mixture,

$$P = P_1 + P_2 = 6.81 + 0.527 = \mathbf{7.337\ atm.}$$

Ex. 8. ***Osmotic pressure of a solution of mannitol in water at 20°C is 5.55 atmosphere. The solution is diluted with an equal volume of water and temperature is raised to 40°C. What will be the osmotic pressure of dilute solution at 40°C?***

Sol. At 20°C, *i.e.*, 293K,

$$P = \frac{n}{mV} RT$$

or $$5.55 = \frac{n}{V} \times 0.0821 \times 293 \qquad \ldots (1)$$

At 40°C, *i.e.*, 313K,

$$P' = \frac{n}{2V} \times 0.0821 \times 313 \qquad \ldots (2)$$

Dividing (2) by (1), we get

$$\frac{P'}{5.55} = \left(\frac{n}{2V} \times 0.0821 \times 313 \right) \div \left(\frac{n}{V} \times 0.0821 \times 293 \right)$$

or $$\frac{P'}{5.55} = \frac{313}{2 \times 293}$$

or $$P' = \frac{313 \times 5.55}{2 \times 293} = \mathbf{2.96\ atm.}$$

Ex. 9. ***A solution containing 8 g of a substance per 100 ml was found to have an osmotic pressure of 500 cm of Hg at 27°C. Calculate the molecular weight of the substance.***

Sol. We have, $w = 8$; $V = 100$ ml $= 0.1$ litre

$$P = 500 \text{ cm} = \frac{500}{76} \text{ atmosphere}$$

$$T = 273 + 27 = 300 \text{ K}$$

We know that,

$$P = \frac{w}{mV} \cdot RT$$

or $$m = \frac{w \cdot RT}{PV} = \frac{8 \times 0.0821 \times 300}{(500/76) \times 0.1} = \mathbf{299.5.}$$

Ex. 10. ***The osmotic pressure of non-volatile solute in benzene at 25°C is 20.66 Nm^{-2}. If the solution had a concentration of 2 g/dm^3, what is the molecular weight of solute ?***

Sol. From solution equation,

$$P = \frac{w}{mV} \cdot RT$$

$P = 20.66 \text{ Nm}^{-2}$, $w = 2$ g, $V = 1 \text{ dm}^3$, $R = 8.31 \text{ Nm}^{-2} \text{ dm}^3 \text{ mol}^{-1}\text{K}^{-1}$, $T = 25 + 273 = 298$ K.

$$\therefore \qquad m = \frac{wRT}{PV}$$

$$= \frac{2 \times 8.31 \times 298}{20.66 \times 1} = \mathbf{239.72}$$

Ex. 11. ***10 g of a substance was dissolved in water and solution made upto 250 c.c. The osmotic pressure of the solution was found to be 600 mm at 15°C. Find the molecular weight of the substance.***

Sol. $P = 600/760$ atm; $T = 15 + 273 = 288$ K; $w = 10$ g; $V = 0.25$ litre

Now, $$P = \frac{w}{mV} \cdot RT$$

or $$m = \frac{w}{PV} \cdot RT$$

$$= \frac{10 \times 0.0821 \times 288}{\frac{600}{760} \times 275}$$

or $$m = \mathbf{119.8}$$

Ex. 12. ***A 1.46% solution of a compound has an osmotic pressure of 783 mm at 30°C. What is the molecular weight of the compound?***

Sol. We know that, $PV = \frac{w}{m} \cdot RT$

or $$m = \frac{w}{PV} \cdot RT$$

We have, $w = 1.46$; $T = 30 + 273 = 303$ K; $V = 0.1$ litre;

$P = 783/760$ atms.

$$\therefore \qquad m = \frac{1.46 \times 0.0821 \times 303}{\frac{783}{760} \times 0.1} = \mathbf{352.52.}$$

Ex. 13. ***The osmotic pressure of a 0.2% solution of an organic compound in water is 570 mm Hg at 12°C. What is the molecular*** **weight of the compound? [$R = 0.0821$ lit atm per degree per mole].**

Sol. We have,

$w = 0.2$; $V = 0.1$ lit; $P = 570/760$ atm; $T - 12 + 273 = 285$ K

Thus, $$PV = \frac{w}{m} . RT$$

or $$m = \frac{w}{PV} . RT$$

$$= \frac{0.2 \times 0.0821 \times 285}{\frac{570}{760} \times 0.1} = \mathbf{62.39.}$$

Ex. 14. ***12.16 g of a substance was dissolved in 100 ml water and its osmotic pressure was found to be 6.92 atmospheres at 15°C. Calculate the molecular weight of the substance.***

Sol. From the equation, $P = \frac{w}{mV} . RT$

We have, $$6.92 = \frac{12.16 \times 0.0821 \times 288}{m \times 0.1} \qquad (\because \ V = 0.1 \text{ litre})$$

or $$m = \frac{12.16 \times 0.0821 \times 288}{6.92 \times 0.1} = 415.49$$

∴ Molecular weight of the substance = **415.49.**

Ex. 15. ***Considering complete dissociation of electrolytes, if O.P. of 1 M urea solution is P, what do you expect the value of O.P. of 1M aluminium sulphate solution ?***

Sol. As aluminium sulphate gives 5 ions on dissociation and as O.P. is proportional to the number of ions, the O.P. of the solution will be 5*P*.

Ex. 16. ***Calculate the value of R in litre-atmosphere, if the osmotic pressure of a solution containing 45 g of sucrose dissolved per litre of solution at 2°C is 3.0 atmospheres.***

Sol. The molecular weight (m) of sucrose ($C_{12}H_{22}O_{11}$)

$$= 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$$

$$T = 2 + 273 = 275 \text{ K}$$

We know that,

$$P = \frac{w}{mV} . RT$$

or
$$R = \frac{P \,.\, wV}{w \,.\, T}$$
$$= \frac{3 \times 342 \times 1}{45 \times 275}$$
$$= \mathbf{0.0829 \text{ litre-atmosphere.}}$$

Ex. 17. ***Calculate the value of constant R from the observation that a solution containing 34.2 g of cane sugar (mol. wt. = 342) in one litre of solution has an osmotic pressure of 2.522 atmospheres at 20°C.***

Sol. $w = 34.2$; $V = 1$; $P = 2.522$; $T = 20 + 273 = 293$ K, $m = 342$; $R = ?$

∴
$$P = \frac{w}{mV} \,.\, RT$$
or
$$R = \frac{P \,.\, mV}{w \,.\, T}$$
$$= \frac{2.522 \times 342 \times 1}{34.2 \times 293}$$
$$= \mathbf{0.0860 \text{ litre atm/degree/mole.}}$$

Ex. 18. ***Calculate the value of R in litre atmosphere if an aqueous solution of 60 g sucrose in one litre has an osmotic pressure of 4 atmosphere.***

Sol.

∴
$$P = \frac{w}{mV} \,.\, RT$$
∴
$$R = \frac{PmV}{RT} = \frac{4 \times 342 \times 1}{60 \times 275}$$
$$= \mathbf{0.0829 \text{ litre atm/deg/mole.}}$$

Problem 8. ***(a) What led van't Hoff to establish the analogy between dilute solution and gases or show that there exists an exact analogy between the dissolved state of a substance and its gaseous state?***

Or, ***State and explain van't Hoff theory of dilute solutions and derive general solution equation for dilute solutions.***
(Meerut 2007, 06)

Or, ***Write a note on van't Hoff theory of dilute solutions.***

(Meerut 2005)

van't Hoff observed the following similarities in the behaviour of dilute solutions and substances in the gaseous state.

(A) Concentration : According to kinetic theory of gases, the molecules of a gas are in a state of constant rapid motion, which results in the concentration of molecules becoming uniform throughout the containing vessel. In dilute solutions too, the molecules of the dissolved solute are in motion and tend to become uniform in concentration. Thus, just as the gas can distribute itself throughout the available space, the solute molecules too get uniformly distributed throughout the solvent medium.

(B) Pressure : The pressure exerted by a gas is due to the bombardment of the molecules on the walls of the containing vessel. Similarly, the osmotic pressure in dilute solutions is also produced due to the bombardment of the solute molecules on the walls of semi-permeable membrane. Just as the gas pressure depends upon the number of gaseous molecules, the osmotic pressure similarly depends upon the solute particles in the solution.

(C) Applicability of laws : van't Hoff showed that various laws which apply to gases, can also be applied to dilute solutions. This led him to formulate the following laws :

1. Boyle-van't Hoff law (First law of osmotic pressure) : *The osmotic pressure (P) of a solution is inversely proportional to the volume (V) of the solution containing one mole of the solute at constant temperature or in other words, osmotic pressure of a solution is directly proportional to concentration (C) at constant temperature.* Thus,

$$P \propto \frac{1}{V} \propto C, \text{ at constant } T$$

This relationship is similar to the mathematical form of the Boyle's law for gases.

2. Charles'-van't Hoff law (Second law of osmotic pressure) : *The osmotic pressure (P) of a solution at constant concentration is directly proportional to temperature (T) on the absolute scale.* Thus,

$$P \propto T, \text{ at constant } C$$

This relationship is similar to the mathematical form of the Charles' law for gases.

3. Avogadro-van't Hoff hypothesis : *At a given temperature, solutions having equal molar concentrations of different solutes have the same osmotic pressure.*

This law is similar to Avogadro's law for gases.

4. Simultaneous effect of concentration and temperature on osmotic pressure : Combining the first and second laws of osmotic pressure for a solution containing one mole of a solute, we obtain an expression :

$$P \propto \frac{T}{V}, \text{ if both } T \text{ and } V \text{ vary}$$

or

$$PV = KT \; (K = \text{constant}) \qquad \ldots (1)$$

van't Hoff obtained the value of K by substituting the values of P, V and T for sucrose solution. He observed that for a solution containing 10 g of sucrose (molecular weight = 342) per litre, the osmotic pressure was found to be 0.66 atmosphere, at 273K. Therefore,

$$K = \frac{PV}{T} = \frac{0.66 \times 34.2}{273} = 0.0821 \text{ lit atm/deg/mole}$$

The value of K is in good agreement with gas constant, R. So, substituting K by universal constant, R, in equation (1), we get,

$$PV = RT$$

In general, if n moles of a solute are dissolved in V litres then the above equation becomes,

$$PV = nRT$$

This equation is known as ***general solution equation.***

The above facts reveal that there exists an exact analogy between the dissolved state of a substance and its gaseous state. van't Hoff thus gave a law which can be stated as under :

'The osmotic pressure of a dilute solution is the same as the pressure, which the solute would exert if present as a gas at the same temperature, occupying the same volume as that of the solution, i.e., gas laws are applicable to dilute solutions.'

This is known as ***van't Hoff law of dilute solutions.***

Problem 9. ***Write a short note on isotonic solutions.***

(Meerut 2006, 05)

Isotonic Solutions

Solutions which have the same osmotic pressures at the same temperature are said to be isotonic. When two solutions having the same osmotic pressures are brought in contact with each other through a semi-permeable membrane, there will thus be no transference of solvent from one solution to the other.

Writing general solution equations for two solutions represented by subscripts 1 and 2, at the same temperature, we get.

$$P_1V_1 = n_1RT = \frac{w_1}{m_1}RT$$

$$P_2V_2 = n_2RT = \frac{w_2}{m_2}RT$$

$$\therefore \quad P_1 = \frac{w_1}{m_1V_1}.RT \text{ and } P_2 = \frac{w_2}{m_2V_2}.RT$$

For isotonic solutions, $P_1 = P_2$

$$\because \quad \frac{w_1}{m_1V_1} = \frac{w_2}{m_2V_2} \qquad \text{... (1)}$$

Thus, according to van't Hoff theory of dilute solution, *isotonic solutions have the same molar concentrations.*

The knowledge of isotonic solutions helps us in determining the molecular weight of a solute. If the molecular weight of one of the substances forming isotonic solutions is known, then that of the other can be calculated with the help of equation (1)*.

NUMERICAL PROBLEMS

Ex. 1. ***A 1.02% solution of glycerine is isotonic with 2% solution of glucose. What is the molecular weight of glycerine?***

Sol. For isotonic solution, we have

$$\therefore \quad \underset{\text{Glycerine}}{\frac{w_1}{m_1V_1}} = \underset{\text{Glucose}}{\frac{w_2}{m_2\,V_2}}$$

$$\text{or} \quad \frac{1.02}{m_1 \times 0.1} = \frac{2}{180 \times 0.1}$$

[Mol. wt. of glucose ($C_6H_{12}O_6$) = 180] or $$m_1 = \frac{180 \times 0.1 \times 1.02}{2 \times 0.1} = \mathbf{91.8.}$$

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* Of the two solutions separated by a s.p.m., if one is of lower O.P., it is said to be ***hypotonic*** relative to the second solution. If it has a higher O.P. than the second solution, it is said to be ***hypertonic*** relative to the second solution.

If red blood cells are put in distilled water (hypotonic solution), water passes into the cells and they swell. If red blood cells are placed in 1% NaCl solution (hypertonic solution), water comes out of the cells and they shrink.

Ex. 2. ***A solution containing 8.6 g/litre of urea (mol. wt. = 60) was found to be isotonic with a 5% solution of an organic solute. Calculate the molecular weight of the solute.***

Sol. For urea : $w_1 = 8.6$; $m_1 = 60$; $V_1 = 1$ litre

For unknown solute : $w_2 = 5$; $m_2 = ?$; $V_2 = 100$ c.c. = 0.1 litre

For isotonic solutions :

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

or $$\frac{8.6}{60 \times 1} = \frac{5}{m_2 \times 0.1}$$

$$m_2 = \frac{60 \times 5 \times 1}{8.6 \times 0.1} = \mathbf{348.83.}$$

Ex. 3. ***Calculate the amount of urea dissolved per litre if its aqueous solution is isotonic with 10% cane sugar solution. Molecular weight of urea = 60.***

Sol. For urea : $w_1 = ?$; $m_1 = 60$; $V_1 = 1$ litre.

For cane sugar : $w_2 = 10$; $m_2 = 342$; $V_2 = 100$ c.c. = 0.1 litre.

For isotonic solutions,

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

or $$\frac{w_1}{60 \times 1} = \frac{10}{342 \times 0.1}$$

or $$w_1 = \frac{60 \times 1 \times 10}{342 \times 0.1} = \mathbf{17.54}$$

Amount of urea = **17.54 g/l.**

Ex. 4. ***de Vries found that 3.42% solution of cane sugar was isotonic with 5.96% solution of raffinose. Calculate the molecular weight of raffinose.***

Sol. For cane sugar : $w_1 = 3.42$; $V_1 = 100$ c.c. = 0.1 litre; $m_1 = 342$.

For raffinose : $w_2 = 5.96$; $V_2 = 100$ c.c. = 0.1 litre; $m_2 = ?$

For isotonic solutions, we have

$$\frac{w_1}{m_1V_1} = \frac{w_2}{m_2V_2} \quad \text{or} \quad \frac{3.42}{342 \times 0.1} = \frac{5.96}{m_2 \times 0.1}$$

or $$m_2 = \frac{5.96 \times 342 \times 0.1}{3.42 \times 0.1} = \mathbf{596}$$

Ex. 5. ***A solution of urea (NH_2CONH_2) is isotonic with a 3% solution of glucose $C_6H_{12}O_6$. Find the concentration of the urea solution.***

Sol. For isotonic solutions,

$$\underset{\text{Urea}}{\frac{w_1}{m_1V_1}} = \underset{\text{Glucose}}{\frac{w_2}{m_2V_2}} \quad \text{or} \quad \frac{w_1}{60 \times 0.1} = \frac{3}{180 \times 0.1}$$

or $$w_1 = \frac{3 \times 60 \times 0.1}{180 \times 0.1} = 1$$

∴ Concentration of urea solution = **1%**

Ex. 6. ***A 5% solution of cane sugar is isotonic with 0.877% solution of urea. Calculate the molecular weight of urea, if molecular weight of cane sugar is 342.***

Solution : For isotonic solutions,

$$\underset{\text{Cane sugar}}{\frac{w_1}{m_1V_1}} = \underset{\text{Urea}}{\frac{w_2}{m_2V_2}}$$

∴ $$\frac{5}{342 \times 0.1} = \frac{0.877}{m_2 \times 0.1}$$

or $$m_2 = \frac{342 \times 0.1 \times 0.877}{5 \times 0.1} = \mathbf{59.98}$$

Ex. 7. ***A solution containing 10 g per litre of an organic substance was found to be isotonic with 2% glucose (mol. wt. = 180) solution. Calculate the molecular weight of the organic compound.***

Sol. For isotonic solutions, we have

$$\underset{\text{O.C.}}{\frac{w_1}{m_1V_1}} = \underset{\text{Glucose}}{\frac{w_2}{m_2V_2}}$$

or $$\frac{10}{m_1 \times 1} = \frac{2}{180 \times 0.1}$$

or $$m_1 = \frac{180 \times 0.1 \times 10}{2 \times 1} = 90$$

∴ Molecular weight of organic compound = **90.**

Ex. 8. ***A solution of 1.73 g of A in 100 ml water is found to be isotonic with a 3.42% solution of sucrose. Calculate the molecular weight of A (25°C).***

Sol. For isotonic solutions,

$$\underset{\text{'A'}}{\frac{w_1}{m_1V_1}} = \underset{\text{Sucrose}}{\frac{w_2}{m_2V_2}}$$

or
$$\frac{1.73}{m_1 \times 0.1} = \frac{3.42}{342 \times 0.1}$$

or
$$m_1 = \frac{1.73 \times 342 \times 0.1}{3.42 \times 0.1} = \mathbf{173.}$$

Problem 10. ***What do you understand by relative lowering of vapour pressure and mole fraction of solute? Enunciate Raoult's law. Describe an experimental method for determining the molecular weight of solute by measuring the lowering of vapour pressure.*** **(Meerut 2006)**

[I] Relative Lowering of Vapour Pressure

It is a well known fact that when a non-volatile solute is dissolved in a liquid, the vapour pressure of the solution becomes smaller than the vapour pressure of the pure solvent. If p and p_s represent the vapour pressures of pure solvent and solution, respectively, then

$$\text{Lowering of vapour pressure} = p - p_s$$

$$\text{Relative lowering of vapour pressure} = \frac{p - p_s}{p}$$

So, relative lowering of vapour pressure is the *ratio of lowering of vapour pressure and the vapour pressure of the pure solvent.*

[II] Mole Fraction of Solute

The mole fraction of solute is defined as the, *'fraction of the total moles of the solute present in the solution, i.e., ratio of moles of the solute to the total number of moles in solution.'*

If n_1 moles of a solute is dissolved in n_2 moles of a solvent, then the total number of moles in the solution will be $(n_1 + n_2)$.

$\therefore$ Mole fraction of solute $= \dfrac{n_1}{n_1 + n_2}$

[III] Statement of Raoult's Law

According to Raoult's law.

'relative lowering of vapour pressure is equal to the mole fraction of the solute.'

Mathematically, $\dfrac{p - p_s}{p} = \dfrac{n_1}{n_1 + n_2}$ ... (1)

For dilute solutions, n_1 is very small as compared so n_2, so it can be neglected. Therefore, equation (1) becomes,

$$\frac{p - p_s}{p} = \frac{n_1}{n_2} \quad \text{... (2)}$$

Equation (2) is Raoult's law equation for dilute solutions.

[IV] Molecular Weight of Solute from Raoult's Law

If w_1 g of a solute of molecular weight m_1 be dissolved in w_2 g of a solvent of molecular weight m_2, then we can write :

$$n_1 = w_1/m_1, \text{ and } n_2 = w_2/m_2$$

Thus, equation (1) becomes :

$$\frac{p - p_s}{p} = \frac{w_1/m_1}{w_1/m_1 + w_2/m_2} \quad \text{... (3)}$$

For dilute solutions, equation (2) becomes :

$$\frac{p - p_s}{p} = \frac{w_1/m_1}{w_2/m_2} = \frac{w_1\, m_2}{w_2\, m_1} \quad \text{... (4)}$$

Thus, if lowering of vapour pressure produced by dissolving a known weight of solute in a known weight of solvent (known molecular weight) is determined, the molecular weight of solute can be calculated.

The measurement of lowering of vapour pressure can be made by a number of methods, *e.g.*, static method (barometric method) etc., but the dynamic method by Walker and Ostwald gives the most accurate results.

Walker and Ostwald method : The apparatus is as shown in figure (10). It consists of two bulbs containing a weighed amount of the solution under study and are connected to the next two bulbs containing a weighed amount of the pure solvent. A weighed

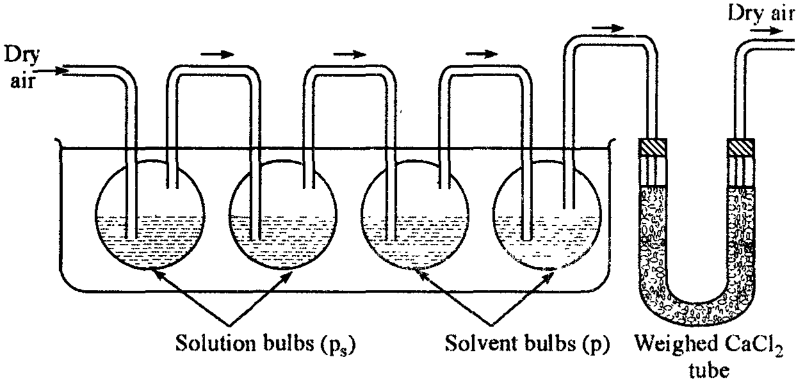

Fig. 10. Walker-Ostwald's apparatus.

amount of anhydrous calcium chloride is taken in an accurately weighed U-tube. All the bulbs must be kept at the same temperature and air must be bubbled gradually to ensure that it gets saturated with the vapour in each bulb. Dry air is bubbled successively through the solution and solvent bulbs as well as U-tube.

Dry air is first bubbled through the solution bulbs. The air as it passes through these bulbs takes up an amount of vapour which is proportional to the vapour pressure (p_s) of the solution at the experimental temperature. As the moist air, saturated upto vapour pressure p_s, passes through the solvent bulbs, it takes up further amount of vapour, which is proportional to the difference in vapour pressure of the pure solvent and the solution. *i.e.*, $p - p_s$. Thus, there will be a loss in the weight of bulbs containing solution and solvent. The air which has been saturated upto a pressure p is now passed through a U-tube containing anhydrous calcium chloride, which in turn absorbs all the water vapours. The calcium chloride tube is weighed at the end of the experiment. The increase in weight of U-tube should be equal to the total loss in the weight of solution and solvent bulbs, which in turn is proportional to p.

Therefore,

$$\text{Loss in weight of solution bulbs} \propto p_s$$

$$\text{Loss in weight of solvent bulbs} \propto p - p_s$$

$$\text{Loss in weight of solution bulbs + Loss in weight of solvent bulbs} \propto p_s + p - p_s \propto p.$$

$$\text{Gain in weight of } CaCl_2 \text{ tube} \propto p$$

$$\therefore \quad \frac{p-p_s}{p} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Loss in weight of (solution + solvent) bulbs}}$$

$$= \frac{\text{Loss in weight of solvent bulbs}}{\text{Gain in weight of CaCl}_2\text{ tube}}$$

Thus, knowing the loss in weight of solution bulbs and solvent bulbs and gain in the weight of $CaCl_2$ tube, we can calculate the relative lowering of vapour pressure.

Thus, the molecular weight (m_1) of the non-volatile solute can be calculated from equation (4) as all the other values are known.

Problem 11. ***Derive Raoult's law equation from the lowering of vapour pressure.***

Derivation of Raoult's Law

According to Wullner, the vapour pressure (p_s) of a solution is directly proportional to the mole fraction of the solvent, *i.e.*,

$$p_s \propto \frac{n_2}{n_1+n_2}$$

or
$$p_s = k \cdot \frac{n_2}{n_1+n_2} \quad \dots (1)$$

where, k = constant.

If $n_1 = 0, p_s = p$.

$\therefore$ From equation (1), $p = k \cdot \frac{n_2}{n_2} = k$

Therefore, equation (1) becomes,

$$p_s = p \cdot \frac{n_2}{n_1+n_2}$$

or
$$\frac{p_s}{p} = \frac{n_2}{n_1+n_2}$$

or
$$1 - \frac{p_s}{p} = 1 - \frac{n_2}{n_1+n_2}$$

or
$$\frac{p-p_s}{p} = \frac{n_1+n_2-n_2}{n_1+n_2} = \frac{n_1}{n_1+n_2}$$

This is Raoult's law for dilute solutions.

Problem 12. ***Show that the lowering of vapour pressure is directly proportional to the osmotic pressure. How can Raoult's law be obtained from their relationship?***

[I] Relation Between Osmotic Pressure and Lowering of Vapour Pressure

Consider a solution contained in an inverted thistle funnel at the end of which is tied a semi-permeable membrane (Fig. 11). The funnel is dipped in a chamber containing solution and the whole chamber is evacuated and is made air tight. The system in the figure cannot represent an equilibrium as the two liquids, *i.e.*, pure water and solution exert different vapour pressures and are in contact with the water vapours. As water vapours exert a higher vapour pressure (p), it will pass through the vapour phase into the solution, having vapour pressure, p_s. This process continues till the two vapour pressures become equal and a state of equilibrium is attained. Due to osmosis, the liquid rises in the tube to a certain height h. The rise in liquid level brings about dilution of the solution. This effect is, however, negligible and the vapour pressure of the solution still remains p_s. At equilibrium, the hydrostatic pressure due to liquid column is equal to the osmotic pressure of the solution. The mathematical derivation of the relation between lowering of vapour pressure (or relative lowering of vapour pressure) and osmotic pressure is carried out as follows:

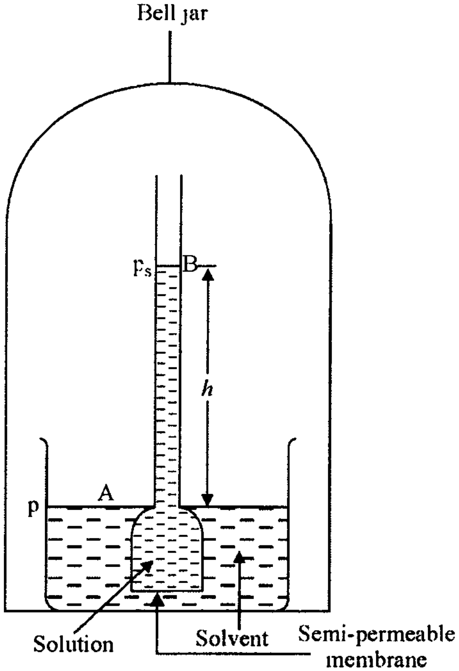

Fig. 11.

Let p and p_s be the vapour pressures of the pure solvent and the solution, respectively and let P be the osmotic pressure of the solution at temperature T of the experiment. The vapour pressure p_s of the solution is equal to the pressure of the vapour of the pure solvent outside the stem at the level of the surface of the solution in the stem, *i.e.*, B.

$$\therefore \qquad p = p_s + hdg$$

or
$$p - p_s = hdg \qquad \dots (1)$$

where, h = height of the column of the solution from the surface of the solvent, d = density of the vapour at the experimental temperature and g = acceleration due to gravity. The osmotic pressure (P) of the solution is given by

$$P = h\rho g \qquad \dots (2)$$

where, ρ = density of the solution and becomes the density of the solvent in the case of a dilute solution.

Dividing equation (1) by equation (2),

$$\frac{p - p_s}{P} = \frac{d}{\rho} \qquad \dots (3)$$

But
$$d = M/V \qquad \dots (4)$$

where, M = molecular weight of solvent and V = molecular volume of vapours.

If the vapour is supposed to obey ideal gas laws, then $pV = RT$, *i.e.*,

$$V = \frac{RT}{p}$$

Then, from equation (4),

$$d = \frac{Mp}{RT}$$

Substituting the value of d in equation (3), we get

$$\frac{p - p_s}{P} = \frac{Mp}{RT\rho}$$

$$\frac{p - p_s}{p} = \frac{MP}{RT\rho} \qquad \dots (6)$$

From equation (6), it is thus clear that the ***osmotic pressure is proportional to lowering of vapour pressure*** $(p - p_s)$ ***or relative lowering of vapour pressure*** $\left(\frac{p - p_s}{p}\right)$.

[II] Deduction of Raoult's Law

From van't Hoff theory of dilute solutions, we have

$$PV = n_1RT$$

or
$$P = \frac{n_1}{V}RT \qquad \dots (7)$$

where, n_1 = number of moles of solute, V = volume of the solvent, P = osmotic pressure and T = absolute temperature.

Since, $$V = \frac{Mn_2}{\rho}$$

where, n_2 = number of moles of solvent. Substituting the value of V in equation (7), we get

$$P = \frac{n_1 RT\rho}{Mn_2}$$

Substituting this value of P in equation (6), we get

$$\frac{p - p_s}{p} = \frac{M}{RT\rho} \cdot \frac{n_1 RT\rho}{Mn_2}$$

or $$\frac{p - p_s}{p} = \frac{n_1}{n_2}$$

This is the modified form of Raoult's law as applicable to dilute solutions, *i.e.*, when $n_1 << n_2$.

NUMERICAL PROBLEMS

Ex. 1. ***A current of dry air was passed through a series of bulbs containing a solution of 3.458g of a substance in 100 g of ethyl alcohol and then through a series of bulb containing pure alcohol. The loss in weight of the former and latter series of bulbs was 0.9675 g and 0.0255 g, respectively. Calculate the molecular weight of the substance.***

Sol. We know that,

$$\frac{p - p_s}{p} = \frac{\text{Loss in weight of solvent bulb}}{\text{Loss in weight of (solvent + solution) bulb}}$$

$$= \frac{0.0255}{0.9675 + 0.0255} = \frac{0.0255}{0.9930}$$

Therefore,

$$\frac{0.0255}{0.9930} = \frac{w_1 m_2}{w_2 m_1} = \frac{3.458 \times 46}{100 \times m_1}$$

(Mol. wt. m_2, of ethyl alcohol = 46)

$$\therefore \quad m_1 = \frac{0.9930 \times 2.458 \times 46}{0.0255 \times 100}$$

$$= \mathbf{61.94.}$$

Ex. 2. ***Dry air was passed successively through a solution of 5 g of a solute in 80.0 g of water and then through pure water. The loss in weight of solution and pure solvent was 2.50 and 0.04 g, respectively. Calculate the molecular weight of the solute.***

Sol.

$$\because \quad \frac{p - p_s}{p} = \frac{\text{Loss in weight of solvent bulb}}{\text{Loss in weight of (solvent + solution) bulb}}$$

$$\therefore \quad \frac{p - p_s}{p} = \frac{0.04}{2.50 + 0.04} = \frac{0.04}{2.54}$$

Now,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or

$$\frac{0.04}{2.54} = \frac{5 \times 18}{80 \times m_1} \qquad \text{(Mol. wt. of water = 18)}$$

or

$$m_1 = \frac{2.54 \times 5 \times 18}{0.04 \times 80} = \mathbf{71.43}$$

Ex. 3. ***A current of dry air was bubbled through a bulb containing 26.66 g of an organic substance in 200 g of water, then through a bulb containing pure water and finally through a tube containing anhydrous calcium chloride. The loss in weight of water bulb = 0.0870 g. Gain in the weight of $CaCl_2$ tube = 2.036 g. Calculate the molecular weight of the organic substance in the solution.***

Sol.

$$\frac{p - p_s}{p} = \frac{\text{Loss in weight of solvent bulb}}{\text{Gain in weight of CaCl}_2\text{ tube}}$$

Now,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or

$$\frac{0.0870}{2.036} = \frac{26.66 \times 18}{200 \times m_1} \qquad (\because \ m_2 = 18)$$

or

$$m_1 = \frac{26.66 \times 18 \times 2.036}{200 \times 0.0870}$$

$$= \mathbf{56.15}$$

Ex. 4. ***A current of dry air was passed through a series of bulb containing a solution of 6.916 g of organic substance in 100 g of alcohol and then through pure alcohol. The loss in weight of former was 0.9675 g and in the latter 0.055 g. Calculate the molecular weight of the solute.***

Sol. We know that;

$$\frac{p - p_s}{p} = \frac{\text{Loss in weight of solvent bulb}}{\text{Loss in weight of (solvent + solution) bulb}}$$

$$= \frac{0.055}{0.9675 + 0.053} = \frac{0.055}{1.0225}$$

Now,

$$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1}$$

or $$\frac{0.055}{1.0225}=\frac{6.916\times 46}{100\times m_1} \qquad (\because \; m_2=46)$$

or $$m_1=\frac{1.0225\times 6.916\times 46}{0.055\times 100}=\mathbf{59.14.}$$

Ex. 5. ***A current of dry air was passed through a solution of 3.50 g of an organic substance in 100 g of a solvent and then through pure solvent alone. The former lost 0.975 g and latter 0.025 g. Calculate the molecular weight of the solute if the molecular weight of solvent is 78.***

Sol. According to Raoult's law,

$$\frac{p-p_s}{p}=\frac{\text{Loss in weight of solvent bulb}}{\text{Loss in weight of (solvent + solution) bulb}}$$

$$=\frac{0.025}{0.025+0.975}=\frac{0.025}{1.000}$$

∴ $$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1} \qquad (m_1=\text{ mol. wt.})$$

or $$0.025=\frac{3.50\times 78}{100\times m_1}$$

or $$m_1=\frac{3.50\times 78}{100\times 0.025}=\mathbf{109.2}$$

Ex. 6. ***The vapour pressure of a solvent at 25°C is 450 mm Hg. When 100 g of a substance is dissolved in 500 g of solvent, the vapour pressure of the solution falls to 423 mm Hg. If the molecular weight of solvent is 74, what is the molecular weight of the solute ?***

Sol. We have $p=450; p_s=423; w_1=100; w_2=500; m_1=?;$ $m_2=74.$

∵ $$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1}$$

∴ $$\frac{450-423}{450}=\frac{100\times 74}{500\times m_1}$$

or $$m_1=\frac{450\times 100\times 74}{500\times 27}=\mathbf{246.6}$$

Ex. 7. ***18.2 g of urea was dissolved in 100 g of water at 50°C. The lowering of vapour pressure produced was 5 mm Hg. Calculate the molecular weight of urea. The vapour pressure of water at 50°C is 92 mm Hg.***

Sol.
$$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1}$$

or
$$\frac{5}{92}=\frac{18.2\times 18}{100\times m_1}$$

or
$$m_1=\frac{18.2\times 18\times 92}{5\times 100}=\mathbf{60.27}$$

Ex. 8. ***The vapour pressure of water at 20°C is 17.50 mm. When 100 g of sucrose is dissolved in 1000 g of water, the vapour pressure is lowered by 0.090 mm. find out the molecular weight of sucrose.***

Sol. We have, $p-p_s=0.090; p=17.50; w_1=100; w_2=1000; m_2=18.$

From Raoult's law of dilute solutions,

$$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1}$$

or
$$\frac{0.090}{17.50}=\frac{100\times 18}{1000\times m_1}$$

or
$$m_1=\frac{100\times 18\times 17.50}{1000\times 0.09}=\mathbf{350.0}$$

Ex. 9. ***The vapour pressure of pure water at 0°C is 4.579 mm of Hg. A solution of lactose containing 8.45 g of lactose in 100 g of water has a vapour pressure of 4.559 mm at the same temperature. Calculate the molecular weight of lactose.***

Sol. We know that

$$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1}$$

or
$$\frac{4.579-4.559}{4.579}=\frac{8.45\times 18}{100\times m_1}$$

or
$$m_1=\frac{8.45\times 18\times 4.579}{100\times 0.02}=\mathbf{348.3}$$

Ex. 10. ***A non-volatile solute was dissolved in water. The weight by weight composition of the solution was 15% and the solution had a vapour pressure of 95.13 kNm^{-2} at the boiling point of solvent at 101.325 k Nm^{-2} pressure. Calculate the molecular weight of the solute.***

Sol. We know that

$$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1}$$

or $$\frac{101.325-95.13}{101.325}=\frac{15\times 18}{100\times m_1}$$

or $$m_1=\frac{15\times 18\times 101.325}{100\times 6.195}$$

$$=\mathbf{44.16}$$

Ex. 11. ***6 g of urea (mol. wt. 60) was dissolved in 180 g of water at 27°C. Calculate the relative lowering of vapour pressure for this solution.***

Sol. According to Raoult's law,

$$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1}$$

$$=\frac{6\times 18}{180\times 60}=0.01$$

∴ Relative lowering of vapour pressure = **0.01**

Ex. 12. ***A solution of 10 g non-volatile solute in 180 g water is prepared. If the molecular weight of the solute is 100 g mol^{-1}, what will be the relative lowering of vapour pressure?***

Sol. $$\frac{p-p_s}{p}=\frac{w_1m_2}{w_2m_1}$$

$$=\frac{10\times 18}{180\times 100}-0.01$$

∴ Relative lowering of V.P. = **0.01**

Ex. 13. ***10 g of a non-volatile solute was dissolved in 100g of acetone (mol. wt. = 58) at 25°C. The vapour pressure of solution was found to be 189.2 mm Hg. Calculate the molecular weight of solute. The vapour pressure of pure acetone at 25°C is 195 mm Hg.***

Sol. We have, $p_s = 189.2$; $p = 195$; $w_1 = 10$; $w_2 = 100$; $m_2 = 58$.

According to Raoult's law,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or
$$\frac{195 - 189.2}{195} = \frac{10 \times 58}{100 \times m_1}$$

or
$$m_1 = \frac{195 \times 10 \times 58}{100 \times 5.8} = \mathbf{195}$$

Ex. 14. ***The vapour pressure of water at 50°C is 92 mm. By dissolving 18.1 g of a substance in 100 g of water, the solution gave vapour pressure which was 87 mm at the same temperature. Calculate the molecular weight of the substance.***

Sol. Given, $p = 92$; $p_s = 87$; $w_1 = 18.1$; $w_2 = 100$; $m_2 = 18$

From Raoult's law,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or
$$\frac{92 - 87}{92} = \frac{18.1 \times 18}{100 \times m_1}$$

or
$$m_1 = \frac{18.1 \times 18 \times 92}{5 \times 100} = \mathbf{59.94}$$

Ex. 15. ***The vapour pressure of water at 20°C is 17 mm. Calculate the vapour pressure of a solution containing 2 g of urea (Mol. wt. = 60) in 60 g of water.***

Sol. According to Raoult's law,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or
$$\frac{17 - p_s}{17} = \frac{2 \times 18}{50 \times 60}$$

or
$$p_s = 17 - \frac{17 \times 2 \times 18}{50 \times 60}$$

$$= 17 - 0.204 = 16.796$$

∴ Vapour pressure of solution = **16.796 mm.**

Ex. 16. ***The relative lowering of vapour pressure of 1% solution of aniline in diethyl ether was found to be 0.008. Calculate the molecular weight of aniline.***

Sol. Given : $\frac{p - p_s}{p} = 0.008$; $w_1 = 1$; $w_2 = 100$.

Molecular weight of diethyl ether ($C_2H_5OC_2H_5$) = 74

According to Raoult's law,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or $$0.008 = \frac{1 \times 74}{100 \times m_1}$$

or $$m_1 = \frac{1 \times 74}{0.008 \times 100} = \mathbf{92.5}$$

Ex. 17. ***At 20°C, the vapour pressure of ether (mol. wt. = 74) is 442 mm. At this temperature, the vapour pressure falls to 426 mm by dissolving 3 g of compound A in 50 g ether. What is the molecular weight of A, if the solution of A in ether is assumed to be very dilute?***

Sol. According to Raoult's law,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

where m_1 = molecular weight of A.

or $$\frac{442 - 426}{442} = \frac{3 \times 74}{50 \times m_1}$$

or $$m_1 = \frac{3 \times 74 \times 442}{50 \times 16} = \mathbf{122.65}$$

Ex. 18. ***The vapour pressure of a solution containing 11.346 g of a non-volatile solute A in 100 g of ether (mol. wt. 74) is 360 mm. If vapour pressure of pure ether is 383 mm, calculate the molecular weight of solute.***

Sol. According to Raoult's law,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or $$\frac{383 - 360}{383} = \frac{11.346 \times 74}{100 \times m_1}$$

or $$m_1 = \frac{11.346 \times 74 \times 383}{100 \times 23} = \mathbf{139.81}$$

Problem 13. ***Deduce the relationship between elevation of boiling point of solvent and molecular weight of the non-volatile solute.***

The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. We know that the vapour pressure of a solution is always lower than that of the pure solvent. Thus, the presence of a non-volatile solute lowers the vapour pressure and to make it boil we have to increase the vapour pressure to the atmospheric pressure by raising the temperature. For a solution, this condition is obtained at a temperature higher than that for the pure solvent. Therefore, *a solution of a non-volatile solute always boils at a higher temperature than the pure solvent.* The difference between the boiling point of a solution and the pure solvent is known as the ***elevation of boiling point*** (ΔT).

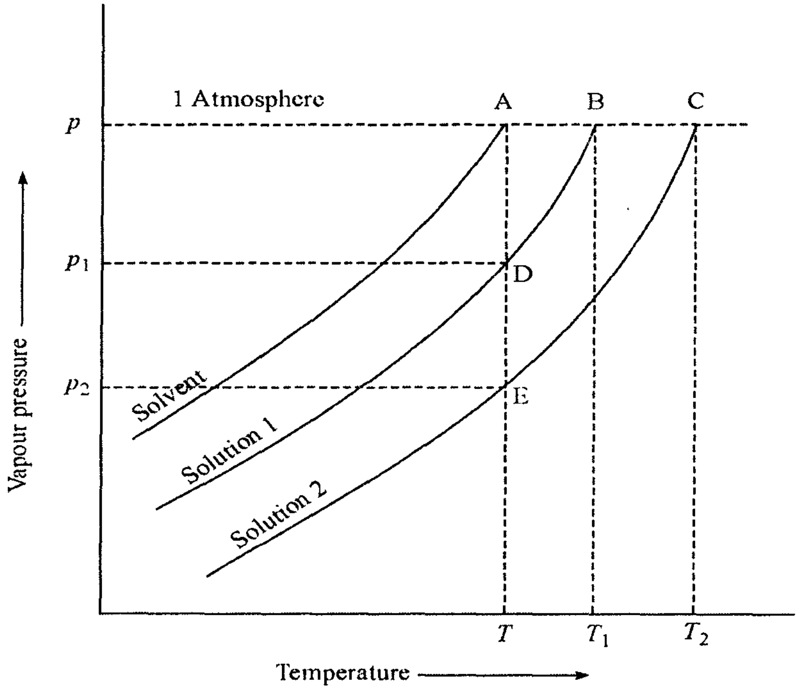

Fig. 12. Vapour pressure and temperature curves.

If we plot the vapour pressure of the pure solvent and two dilute solutions of different concentration (say 1 and 2) against temperature, a set of curves are obtained as shown in figure (12). If atmospheric pressure is represented by line pC, then boiling points of pure solvent, solution 1 and solution 2 will be T, T_1 and T_2, respectively.

For very dilute solutions, the curves are nearly parallel straight lines. The triangles ABD and ACE are similar. Thus,

$$\frac{AB}{AC} = \frac{AD}{AE}$$

or
$$\frac{T_1 - T}{T_2 - T} = \frac{p - p_1}{p - p_2}$$

where, p, p_1 and p_2 are the vapour pressures of pure solvent, solution 1 and solution 2, respectively.

If Δp and ΔT represent the respective lowering of vapour pressure and elevation of boiling point, then,

$$\frac{\Delta T_1}{\Delta T_2} = \frac{\Delta p_1}{\Delta p_2}$$

or
$$\Delta T \propto \Delta p$$

Thus, the ***elevation of boiling point is proportional to the lowering of vapour pressure.***

For dilute solutions, Raoult's law can be written as,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or
$$\Delta p = \frac{w_1 m_2}{w_2 m_1} \cdot p \qquad \dots (1)$$

where, p = vapour pressure of pure solvent, p_s = vapour pressure of solution, w_1 = weight of solute of molecular weight m_1, w_2 = weight of solvent of molecular weight m_2.

For the same solvent, m is constant and p, the vapour pressure at the boiling point is also constant. So,

$$\Delta p = pm_2 \cdot \frac{w_1}{w_2 m_1} = \text{constant} \times \frac{w_1}{w_2 m_1}$$

$$\therefore \qquad \Delta p \propto \frac{w_1}{w_2 m_1}$$

But we know that, $\Delta p \propto \Delta T$

$$\Delta T \propto \frac{w_1}{w_2 m_1}$$

or
$$\Delta T = k \cdot \frac{w_1}{w_2 m_1} \qquad \dots (2)$$

where, k is a constant known as ***boiling point constant.***

If $w_1/m_1 = 1$ and $w_2 = 1$ g, then from equation (2)

$$k = \Delta T$$

So, ***boiling point constant*** is defined as *the elevation in boiling point produced by dissolving 1 mole of a solute in 1 g of a solvent.*

If $w_1/m_1 = 1$ and $w_2 = 100$ g, then from equation (2),

$$\frac{k}{100} = \Delta T$$

or K_{100} or $K = \Delta T$, where $k = 100\,K$ or $100\,K_{100}$

where, K or K_{100} is another constant, known as ***molecular elevation constant.*** It is defined as, the *elevation in boiling point produced by dissolving 1 mole of a solute in 100 g of a solvent.*

Thus, replacing k by K in equation (2), we get

$$\Delta T = \frac{100\,Kw_1}{w_2 m_1} \qquad \dots (3)$$

If $w_1/m_1 = 1$ and $w_2 = 1000$ g, then from equation (2),

$$\frac{k}{1000} = \Delta T$$

or $K_b = \Delta T$, where $k = 1000K_b$

where, K_b is a constant, known as ***molal elevation constant*** or ***ebullioscopic constant***. It is defined as, *the elevation in boiling point produced by dissolving 1 mole of a solute in 1000 g of a solvent.*

Replacing k by K_b in equation (2), we get,

$$\Delta T = \frac{1000\,K_b w_1}{w_2 m_1} \qquad \dots (4)$$

Equations (2), (3) and (4) are different expressions connecting the elevation in boiling point and molecular weight of dissolved substance.

Problem 14. ***From thermodynamics point of view, derive a relation between elevation of boiling point and molecular weight of a non-volatile solute.***

Or, From thermodynamics point of view, derive a relation between lowering of vapour pressure and elevation of boiling point.

It is a well known fact that the boiling point of the pure solvent is elevated when a non-volatile solute is added to it. If a vapour pressure-temperature curve is drawn then the curves as shown in figure (13) are obtained. The three curves are for pure solvent, dilute solution I and dilute solution II, respectively. Evidently, T the temperature at which the vapour pressure (p) of the solvent is equal to the atmospheric pressure gives the boiling point of the pure solvent.

The vapour pressure of solution I at the same temperature T_1 is p_1 which is, however, less than the atmospheric pressure. It will not boil at this temperature. As seen from the figure, the solution I will boil at a temperature T_1 when its vapour pressure also rises to p. Similarly, T_2 is the boiling point of solution II when its vapour pressure (p_2) becomes equal to p.

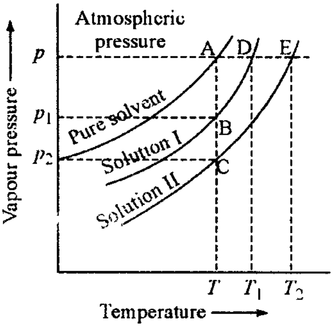

Fig. 13. Vapour pressure-temperature curves.

For liquid-vapour equilibrium Clausius-Clapeyron equation can be written in the form,

$$\frac{d \log p}{dT} = \frac{L_e}{RT^2}$$

or

$$\frac{dp}{p} = \frac{L_e}{RT^2} \cdot dT \qquad \ldots (1)$$

where $\Delta H_V = L_e$ = latent heat of evaporation of 1 mole of solvent from the solution.

Assuming L_e to be constant over a small range of temperature near the boiling point, we integrate equation (1) between temperature limits T and T_1 and vapour presure p_1 and p. Thus,

$$\int_{p_1}^{p} \frac{dp}{p} = \int_{T}^{T_1} \frac{L_e}{RT^2} \cdot dT$$

$$\log_e \frac{p}{p_1} = \frac{L_e}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

$$= \frac{L_e}{R}\left(\frac{T_1 - T}{TT_1}\right) \qquad \ldots (2)$$

Evidently, $(T_1 - T)$ is the elevation in boiling point which is represented by ΔT. Further, for a dilute solution, T and T_1 are not far apart from each other, *i.e.*, $T \approx T_1$. So, equation (2) can be written in the following form, though approximately. So,

$$\log_e \frac{p}{p_1} = \frac{L_e}{R} \cdot \frac{\Delta T}{T^2} \qquad \ldots (3)$$

Now, $\log_e \dfrac{p}{p_1} = -\log_e\left(1 - \dfrac{p - p_1}{p}\right) = -\left(-\dfrac{p - p_1}{p}\right)$

or $$\log_e \frac{p}{p_1} = \frac{p - p_1}{p} \quad \{\text{As } \log(1 - x) = -x, \text{ when } x \text{ is small}\}$$

Therefore, equation (3) becomes,

$$\frac{p - p_1}{p} = \frac{L_e}{R} \cdot \frac{\Delta T}{T^2} \qquad \dots (4)$$

From equation (4), it is clear that ***lowering of vapour pressure (p − p₁) is proportional to the elevation of boiling point,*** ΔT. As proved already, the lowering of vapour pressure is also proportional to the osmotic pressure. Hence, the ***elevation of boiling point is also proportional to osmotic pressure.***

According to Raoult's law, the relative lowering of vapour pressure is equal to the mole fraction of solute. In case of a dilute solution, we have

$$\frac{p - p_1}{p} = \frac{n_1}{n_2}$$

where, n_1 and n_2 are the number of moles of solute and solvent, respectively and p_1 is the vapour pressure of the solution. So, equation (4) reduces to

$$\frac{n_1}{n_2} = \frac{L_e}{R} \cdot \frac{\Delta T}{T^2}$$

or $$\Delta T = \frac{RT^2}{L_e} \cdot \frac{n_1}{n_2}$$

If $w_1\,g$ of solute be dissolved in $w_2\,g$ of solvent, then,

$$n_1 = \frac{w_1}{m_1} \quad \text{and} \quad n_2 = \frac{w_2}{m_2}$$

where, m_1 and m_2 are the molecular weights of solute and solvent, respectively. So,

$$\Delta T = \frac{RT^2}{L_e} \cdot \frac{w_1/m_1}{w_2/m_2} = \frac{RT^2}{L_e} \cdot \frac{w_1 m_2}{w_2 m_1} \qquad \dots (5)$$

If l_e is the latent heat of vaporisation per gram of solvent then $l_e = \frac{L_e}{m_2}$. So, equation (5) can be written as

$$\Delta T = \frac{RT^2 w_1}{l_e\, w_2 m_1} \qquad \dots (6)$$

For a given solvent at its boling point T and l_e are constants. So, from equation (6) or $$\Delta T = \text{constant} \times \frac{w_1}{w_2\, m_1}$$

or $$\Delta T = \frac{k w_1}{w_2 m_1} \qquad \ldots (7)$$

where k is constant known as *elevation constant.* If $\frac{w_1}{m_1} = 1$ and $w_2 = 1\,g$ then $k = \Delta T$. So, elevation constant is defined as the ***elevation in bciling point produced by disolving 1 g of solute in 1 g of solvent.***

If 1 mole of a solute is dissolved in 100 g of the solvent, *i.e.*, $\frac{w_1}{m_1} = 1$, $w_2 = 100$, then equation (5) becomes,

$$\Delta T = \frac{RT^2}{l_e \,.\, 100} = K \text{ or } K_{100} \qquad \ldots (8)$$

where K is known as *molecular elevation constant.* K or K_{100} is defined as the ***elevation of boiling point produced by dissolving 1 mole of a solute in 100 g of solvent.***

Therefore, combining equations (6) and (8), we get

$$\Delta T = \frac{100\, K w_1}{w_2 m_1} \qquad \ldots (9)$$

If 1 mole of a solute is dissolved in 1000 g of the solvent then,

$$\Delta T = \frac{RT^2}{1000\, l_e} = K_b \qquad \ldots (10)$$

where K_b is known as *molal elevation constant.* K_b is thus defined as the ***elevation of boiling point produced by dissolving 1 mole of a solute in 1000 g of solvent.'***

Therefore, combining equations (6) and (10), we get

$$\Delta T = \frac{1000\, K_b\, w_1}{w_2 m_1} \qquad \ldots (11)$$

Equations (7), (9) and (11) are the required relations between elevation of boiling point and molecular weight of solute.

Problem 15. ***(i) Define molal elevation constant.***

(Meerut 2007, 05)

(ii) How molal elevation constant is related to latent heat of vaporisation? Describe the method used for determining the molecular weight of a non-volatile solute by the boiling point method.

[I] Molal Elevation Constant (K_b)

It is defined as the '*elevation in boiling point produced by dissolving one mole of a solute in 1000 g or 1 kg of a solvent.*' For example, K_b for water is 0.518° which means that when 1 mole of any solute is dissolved in 1000 g of water the elevation of boiling point will be 0.518°.

[II] Relation Between Molal Elevation Constant (K_b) and Latent Heat of Vaporisation (L_e)

van't Hoff showed that by thermodynamical reasoning, we can obtain the following expression :

$$K_b = \frac{RT^2}{1000L_e}$$

where, $T =$ boiling point of the solvent on the absolute scale, $R =$ gas constant and $L_e =$ latent heat of vaporisation per gram of solvent. As $R = 2$ calories,

$$K_b^* = \frac{0.002T^2}{L_e}$$

The unit of K_b is degree.

[III] Determination of Molecular Weight of a Non-Volatile Solute

Though a number of methods, *e.g.*, Beckmann's method. Cottrell's method etc. are available for determining the molecular weight of a non-volatile solute, the most convenient method generally employed in the laboratory is ***Landsberger's method.***

In Landsberger's method, the liquid is heated to its boiling point by passing the vapours of the pure boiling solvent into it. When the vapour is condensed, it gives out its latent heat of vaporisation which heats the liquid to its boiling point without any danger of super-heating.

The apparatus (Fig. 14) consists of a vapour generating flask in which solvent is taken and boiled. An inner boiling tube is taken and has a bulb with a hole in the side and is graduated in mL. It

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* In case of water, $T = 100 + 273 = 373\ K$; $L_e = 537$ calories and so

$$K_b = \frac{0.002 \times 373 \times 373}{537} = 0.518^\circ$$

is fitted with an accurate thermometer (graduated to 0.01°) and a glass tube with a bulb blown at the end which has many holes in it. This bulb is known as *rose head.* It ensures uniform distribution of solvent vapours into the solvent. The inner tube is surrounded by an outer jacket which receives hot vapours from the inner tube through the hole. This jacket forms a protecting jacket and prevents loss of heat from the inner tube due to radiation and it further protects it from draughts of air.

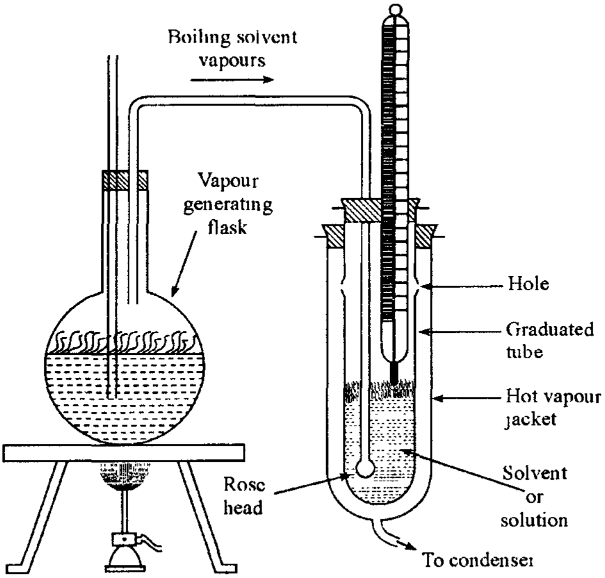

Fig. 14. Landsberger's apparatus.

In the actual experiment, about 7-8 ml of pure solvent is taken in the inner tube and vapours from vapour generating flask are passed into it. After sometime the liquid begins to boil. As soon as the temperature becomes constant, the thermometer reading is taken. This gives the boiling point (T) of the pure solvent. Now the supply of solvent vapour is cut off temporarily and a weighed amount (w_1) (say 0.5–1.0 g) of a non-volatile solute whose molecular weight is to be determined is added into the inner tube. The boiling point (T_1) of the solution is then taken as before. Immediately after the temperature is read off, the rose-head and thermometer are raised out of the solution and the volume of the solution noted.

The molecular weight (m_1) of the non-volatile solute is then calculated by the expression :

$$\Delta T = \frac{1000 K_b w_1}{w_2 m_1}$$

or $$m_1 = \frac{1000 K_b\, w_1}{w_2 \,.\, \Delta T}$$

Knowing all the values of right hand side, we can easily calculate m_1.

NUMERICAL PROBLEMS

Ex. 1. ***(a) Calculate the value of K_b for water given that pure water boils at 100° C and latent heat of its vaporisation is 540 cal g^{-1} (R = 2 calories).*** **(Meerut 2005)**

(b) Calculate the molal elevation constant for water. The latent heat of vaporisation is 536 calories per gram.

Sol. (a) Boiling point of water

$$(T) = 100^\circ\text{C} = 100 + 273 = 373 \text{ K}$$

Latent heat of vaporisation of water (L_e) = 540 cal/g.

$$\therefore \qquad K_b = \frac{RT^2}{1000 L_e} = \frac{2 \times (373)^2}{1000 \times 540} = \mathbf{0.515^\circ}$$

(b) We know that,

$$K_b = \frac{RT^2}{1000 L_e} = \frac{2 \times (373)^2}{1000 \times 536} = \mathbf{0.52^\circ}$$

Ex. 2. ***A solution containing 2.44 g of a solute dissolved in 75 g of water boiled at 100.413°C. Calculate the molecular weight of the solute. (K_{1000} = 0.52°C).***

Sol. $w_1 = 2.44$; $w_2 = 75$; $m_1 = ?$; $\Delta T = 100.413 - 100 = 0.413^\circ$

$$\therefore \qquad \Delta T = \frac{1000 K_b w_1}{w_2 m_1}$$

or $$m_1 = \frac{1000 K_b w_1}{w_2 \,.\, \Delta T}$$

$$= \frac{1000 \times 0.52 \times 2.44}{75 \times 0.413} = \mathbf{40.96}$$

Ex. 3. ***On dissolving 0.51 g of a substance A in 30.0 g of chloroform, its boiling point was raised by 0.30°C. The molal elevation constant of chloroform is 3.9°C per 1000 g of chloroform. Find the molecular weight of A.***

Sol. $w_1 = 0.51; w_2 = 30; m_1 = ?; \Delta T = 0.30; K_b = 3.9^\circ$.

We know that, $$m_1 = \frac{1000 K_b w_1}{w_2 \cdot \Delta T} = \frac{1000 \times 3.9 \times 0.51}{30 \times 0.30} = \mathbf{221}$$

Ex. 4. ***3 g of camphor added to 25.2 g of chloroform raised the boiling point of the solvent by 0.299°C. Calculate the molecular weight of camphor, if K_b of chloroform is 0.38°.***

Sol. $w_1 = 3.0; w_2 = 25.2; m_1 = ?; \Delta T = 0.299^\circ; K_b = 3.80^\circ$

Now, $$\Delta m = \frac{1000 K_b w_1}{w_2 \cdot \Delta T} = \frac{1000 \times 0.38 \times 3}{25.2 \times 0.299} = \mathbf{151.39}$$

Ex. 5. ***The molal elevation constant for water is 0.52°. At what temperature will a solution contain 5.60 g of glucose per litre boil?***

Sol. $w_1 = 5.6; w_2 = 1000; m_1 = 180; T = ?; K_{1000} = 0.52^\circ$.

Now, $$\Delta T = \frac{1000 K_b w_1}{w_2 \cdot m_1} = \frac{1000 \times 0.52 \times 5.6}{1000 \times 180} = \mathbf{0.0161}$$

$\therefore$ Boiling point of solution = B.pt. of solvent + ΔT

= 100 + 0.0161 = **100.0161°C**

Ex. 6. ***Calculate the boiling point of a solution containing 0.4560 g of camphor (mol. wt. = 152) dissolved in 31.4 g of acetone (b. pt. = 56.30°C), if the elevation constant per 1000 g of acetone is 1.72°.***

Sol. $w_1 = 0.4560; w_2 = 31.4; \Delta T = ?; m_1 = 152; K_{1000} = 1.72^\circ$.

Now, $$\Delta T = \frac{1000 K_b w_1}{w_2 \cdot m_1} = \frac{1000 \times 1.72 \times 0.4560}{31.4 \times 152} = \mathbf{0.14}$$

$\therefore$ Boiling point of the solution = 56.30 + 0.164 = **56.464°C**

Ex. 7. ***A solution of 1 g phenol in 50 ml of ether (density = 0.714) boiled at a temperature 0.63° higher than the boiling point of ether. The molal elevation constant of ether is 2.12°. Calculate the molecular weight of phenol.***

Sol. Now, $$m_1 = \frac{1000 K_b w_1}{w_2 \cdot \Delta T} = \frac{1000 \times 2.12 \times 1.0}{50 \times 0.714 \times 0.63} = \mathbf{94.26}$$

Ex. 8. ***The boiling point of acetone is 56.38° C. A solution of 0.564 g of a compound in 16 g of acetone boiled at 56.75°C. What is the molecular weight of the compound? (Molecular elevation for acetone = 1.67° per 1000 g).***

Sol. We know that :

$$m_1 = \frac{1000 K_b w_1}{w_2 \,.\, \Delta T}$$

Here, $K_b = 1.67$; $w_1 = 0.564$; $w_2 = 16$; $\Delta T = 56.75 - 56.38 = 0.37^\circ$

$$\therefore \qquad m_1 = \frac{1000 \times 1.67 \times 0.564}{16 \times 0.37} = \mathbf{159.1}$$

Ex. 9. ***10 g of substance dissolved in 100 g of water raised its boiling point by 0.98°C. Calculate the molecular weight of the substance. Molecular elevation constant for 1000 g of water*** **= 0.52°.**

Sol. We know that :

$$m_1 = \frac{1000 K_b w_1}{w_2 \,.\, \Delta T}$$

Here, $K = 5.2$; $w_1 = 10$; $w_2 = 100$; $\Delta T = 0.98$.

$$\therefore \qquad m_1 = \frac{1000 \times 0.52 \times 10}{100 \times 0.98} = \mathbf{53.06}$$

Ex. 10. ***The boiling point of acetone is 56.38° at 750 mm barometric pressure. Solution of 0.707 g of a compound in 10g of acetone boils at 56.88°. What is the molecular weight of the compound? Molecular elevation constant for acetone is 1.67° for 1000 g of solvent.***

Sol. We know that :

$$m_1 = \frac{1000 K_b w_1}{w_2 \,.\, \Delta T}$$

Here, $K_b = 1.67$; $w_1 = 0.707$; $w_2 = 10$; $\Delta T = 56.88 - 56.38 = 0.5^\circ$

$$\therefore \qquad m_1 = \frac{1000 \times 1.67 \times 0.707}{10 \times 0.5} = \mathbf{236.13}$$

Ex. 11. ***Calculate the molecular weight of the compound if the addition of 1.0 g of this compound to 50 g of benzene raises the boiling point of benzene by 0.3° C. K_b for 1000 g of benzene is 2.58°.***

Sol. We know that :

$$m_1 = \frac{1000 K_b w_1}{w_2 \,.\, \Delta T}$$

Here, $K_b = 2.58$; $w_1 = 1.0$; $w_2 = 50$; $\Delta T = 0.3$

$$\therefore \qquad m_1 = \frac{1000 \times 2.58 \times 1}{50 \times 0.} = \mathbf{172}$$

Ex. 12. ***The boiling point of chloroform is increased by 0.323°C by dissolving 1.0286 g of a substance in 70 g of chloroform. Calculate the molecular weight of the substance, (K_b = 3.9°C).***

Sol. We know, $m_1 = \dfrac{1000K_b w_1}{w_2 \Delta T}$

$$= \frac{1000 \times 3.9 \times 1.0286}{70 \times 0.323} = \mathbf{177.42}$$

Ex. 13. ***Molal elevation constant of chloroform is 3.63 kg mole^{-1}. A solution of some organic solute in this solvent boils at 0.15 K higher than chloroform. What is the molality of the solution ?***

Sol. Molality of a solution is defined as the number of moles of solute (w_1/m_1) dissolved in 1000 g or 1 kg of solvent.

We know that, $\Delta T = \dfrac{1000K_b w_1}{w_2 m_1}$ or $\dfrac{w_1}{w_2 m_1} = \dfrac{\Delta T}{1000K_b}$

or $$\frac{w_1}{m_1 \times 1000} = \frac{0.15}{1000 \times 3.63} = 0.041$$

$\therefore$ Molality = **0.041 m**

Ex. 14. ***The latent heat of vaporisation of CS_2 is 85.9 cal and its boiling point 46.2°C. The solution of 0.938 g of benzoic acid in 50.0 g CS_2 boiled at 47.387°C. Calculate the molecular weight of benzoic acid in the solution.***

Sol. We have : $L_e = 85.9$; $T = 46.2 + 273 = 319.2$ K; $m_1 = ?$; $w = 0.938$; $w_2 = 50.0$; $\Delta T = 47.387 - 46.20 = 1.187°$

We know that, $K_b = \dfrac{RT^2}{1000L_e} = \dfrac{2 \times (319.2)^2}{1000 \times 85.9} = 2.372$

Now, $m_1 = \dfrac{1000K_b\, w_1}{w_2 \,.\, \Delta T} = \dfrac{1000 \times 2.372 \times 0.938}{50 \times 1.187} = \mathbf{37.48}$

Ex. 15. ***A solution containing 6.0 g of a solute dissolved in 250 ml of water gave an osmotic pressure of 4.5 atmospheres at 27°C. Calculate the boiling point of the solution. The molal elevation constant for water is 0.52°.***

Sol. From the first part of the question, we will calculate the molecular weight of the solute by means of the equation

$$P = \frac{w}{mV} \,.\, RT \qquad \ldots (1)$$

$P = 4.5$; $w = 6.0$; $m = ?$; $V = 0.25$ litre; $R = 0.0821$; $T = 273 + 27 = 300$ K

$$\therefore \qquad m = \frac{wRT}{PV} = \frac{6 \times 0.0821 \times 300}{4.5 \times 0.25} = 131.3$$

For the second part of the question, we have

$$\Delta T = \frac{1000 K_b\, w_1}{w_2 \,.\, m_1} = \frac{1000 \times 0.52 \times 6}{250 \times 131.3} = 0.095^\circ$$

$\therefore$ Boiling point of solution. = B. pt. of solvent + ΔT

$$= 100 + 0.095$$

$$= \mathbf{100.095^\circ C}$$

Problem 16. ***Derive a relationship between the depression of freezing point and the molecular weight of a non-volatile solute.***

The freezing point of a liquid is that temperature at which the liquid form and its solid form remain in equilibrium. This is so when vapour pressures of both the forms are equal at the same temperature. Therefore, *freezing point of a liquid is that temperature at which the vapour pressures of the liquid and that of its solid form become equal.*

The lowering of vapour pressure due to dissolving of a solute causes the solution to freeze at a lower temperature, because at the freezing point of a liquid, its vapour pressure becomes equal to that of its solid form which separates out and is in equilibrium with its liquid phase. The solid form has a higher vapour pressure when it remains in equilibrium with the pure solvent at its freezing point. So, it may be concluded that the *freezing point of the solution is less than that of the pure solvent.* The difference between the freezing points of solvent and solution is called the *depression in freezing point* (ΔT).

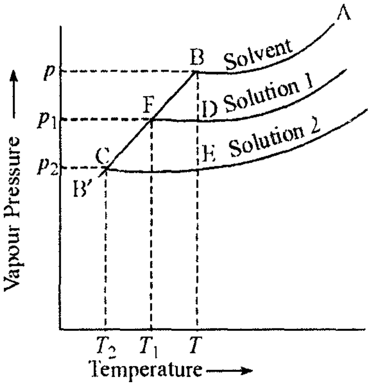

Fig. 15. Vapour pressure-temperature curves.

On plotting a graph between the vapour pressure and temperature for a pure solvent, we get a curve AB (Fig. 15). There is a sharp break in the curve at B, below which the vapour pressure-temperature curve exhibits a sharp decrease in vapour pressure with a decrease in temperature. This indicates the existence of a solid along the part BB′ of the curve. At B, the liquid and solid phases co-exist and thus the temperature (T) corresponding to this point is the freezing point of the pure solvent. The vapour pressure-temperature curves for solutions 1 and 2 of different concentrations are as shown. Points F and C correspond to the freezing points of the solutions 1 and 2 which are T_1 and T_2, respectively.

For very dilute solutions, the curves are nearly parallel straight lines. The triangles BFD and BCE are similar. Thus,

$$\frac{\mathrm{FD}}{\mathrm{CE}} = \frac{\mathrm{BD}}{\mathrm{BE}}$$

or

$$\frac{T - T_1}{T - T_2} = \frac{p - p_1}{p - p_2}$$

where, p, p_1 and p_2 are the vapour pressures of pure solvent, solution 1 and solution 2, respectively.

If Δp and ΔT represent the lowering of vapour pressure and depression in freezing point, respectively, then

$$\frac{\Delta T_1}{\Delta T_2} = \frac{\Delta p_1}{\Delta p_2}$$

or

$$\Delta I \propto \Delta p$$

Thus, the ***depression in freezing point is proportional to the lowering of vapour pressure.***

For dilute solutions, Raoult's law can be written as

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or

$$\Delta p = \frac{w_1 m_2}{w_2 m_1} \cdot p \qquad \text{... (1)}$$

where, $p =$ vapour pressure of the pure solvent, $p_s =$ vapour pressure of solution, $w_1 =$ weight of solute of molecular weight m_1, $w_2 =$ weight of solvent of molecular weight m_2.

For the same solvent, m_2 is constant and p, the vapour pressure at the freezing point is also constant. So,

$$\Delta p = p m_2 \cdot \frac{w_1}{w_2 m_1} = \text{constant} \times \frac{w_1}{w_2 m_1}$$

$$\therefore \qquad \Delta p \propto \frac{w_1}{w_2 m_1}$$

But we know that $\Delta p \propto \Delta T$

$$\therefore \qquad \Delta T \propto \frac{w_1}{w_2 m_1}$$

or $$\Delta T \propto \frac{kw_1}{w_2 m_1} \qquad \dots (2)$$

where, k is a constant known as ***freezing point constant*** for the solvent.

If $w_1/m_1 = 1$ and $w_2 = 1$ g, then from equation (2), $k = \Delta T$

So, freezing point constant is defined as, the *depression in freezing point produced by dissolving 1 mole of solute in 1 g of a solvent.*

If $w_1/m_1 = 1$ and $w_2 = 100$ g, then from equation (2),

$$\Delta T = \frac{k}{100} = K \text{ or } K_{100}$$

or $$k = 100K \text{ or } 100K_{100}$$

where, K or K_{100} is another constant, known as molecular depression constant. It is defined as, *the depression in freezing point produced by dissolving 1 mole of solute in 100 g of a solvent.*

Thus, replacing k by K in equation (2), we get

$$\Delta T = \frac{100\,Kw_1}{w_2 m_1} \qquad \dots (3)$$

If $w_1/m_1 = 1$ and $w_2 = 1000$ g, then from equation (2),

$$\Delta T = \frac{k}{1000} = K_f \text{ or } K_{1000} \quad \text{where } k = 1000K_f = 1000K_{1000}$$

where, K_f (or K_{1000}) is a constant known as ***molal depression constant*** or ***cryoscopic constant***. It is defined as, the *depression in freezing point produced by dissolving 1 mole of solute in 1000 g of a solvent.*

Thus, replacing k by K_f in equation (2), we get

$$\Delta T = \frac{1000K_f w_1}{w_2 m_1} \qquad \dots (4)$$

Equations (2), (3) and (4) are different expressions connecting the depression in freezing point and molecular weight of a dissolved substance.

Problem 17. ***From thermodynamics point of view, derive a relation between depression of freezing point and molecular weight of a non-valatile solute.***

Or, From thermodynamics point of view derive a relation between the lowering of vapour pressure and depression in freezing point.

The lowering of vapour pressure due to dissolving a solute causes the solution to freeze at a lower temperature. This is because at the freezing point of the liquid, its vapour pressure becomes equal to the vapour pressure of its solid form which separates out and remains in equilibrium with the liquid phase. This solid phase has a higher vapour pressure when it remains in equilibrium with the pure solvent at its freezing point. So, it may be concluded that the freezing point of a solution is always less than that of the pure solvent.

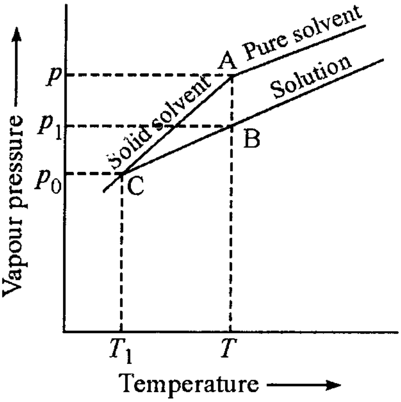

Fig. 16. Vapour pressure-temperature curves.

The above fact is clearly shown in fig. (16) in which vapour pressure-temperature curves of the pure solvent, solid solvent and dilute solution are given. In the figure, the vapour pressure curves of a solvent in the liquid and solid states, are seen to meet at the point A. Then, at the corresponding temperature T, the solid and liquid states have the same vapour pressures. Therefore, T represents the freezing point of the solvent. As the vapour pressure of the solution is less than that of the pure solvent, the vapour pressure curve of the solution always lies below that of the pure solvent. This curve is seen to meet the vapour pressure curve of the solvent at the point C, which lies below A. Therefore, T_1 which lies below T, gives the freezing point of the solution. Evidently, $(T - T_1)$ represents the depression in freezing point of solution.

For liquid-vapour equilibrium, Clausius-Clapeyron equation can be written in the following form

$$\frac{d \log p}{dT} = \frac{L_e}{RT^2}$$

or

$$\frac{dp}{p} = \frac{L_e}{RT^2} dT \qquad \dots (1)$$

where L_e is the latent heat of vaporisation for 1 mole of solvent.

Integrating equation (1) between proper limits, we have,

$$\int_{p_1}^{p_0} \frac{dp}{p} = \int_{T}^{T_1} \frac{L_e}{RT^2} dT$$

or $$\log \frac{p_0}{p_1} = \frac{L_e}{R}\left(-\frac{1}{T_1} + \frac{1}{T}\right)$$

or $$\log \frac{p_0}{p_1} = \frac{L_e}{R}\left(\frac{T_1 - T}{TT_1}\right) \quad \text{... (2)}$$

where, p_0 is the vapour pressure of the solution at T and p_1 is the vapour pressure of the solution at B.

Similarly, for solid-vapour equilibrium, we have,

$$\log_e \frac{p_0}{p} = \frac{L_s}{R}\left(\frac{T_1 - T}{TT_1}\right) \quad \text{... (3)}$$

where, L_s is the molar latent heat of sublimation of the solid.

Subtracting equation (2) from (3), we get,

$$\log_e \frac{p_1}{p} = \frac{L_s - L_e}{R}\left(\frac{T_1 - T}{TT_1}\right)$$

or $$\log_e \frac{p_1}{p} = \frac{L_f}{R}\left(\frac{T_1 - T}{TT_1}\right) \quad \text{... (4)}$$

where L_f is the molar latent heat of fusion and is equal to $(L_s - L_e)$.

As T is greater than T_1, therefore, equation (4) can be written as,

$$\log_e \frac{p}{p_1} = \frac{L_f}{R}\left(\frac{T - T_1}{TT_1}\right)$$

or $$\log_e \frac{p}{p_1} = \frac{L_f}{R} \cdot \frac{\Delta T}{TT_1} \qquad [\text{As } T - T_1 = \Delta T]$$

The values of T and T_1 are close to one another, because the solution is dilute. So, we can write $T = T_1$, therefore,

$$\log_e \frac{p}{p_1} = \frac{L_f}{R} \cdot \frac{\Delta T}{T^2} \quad \text{... (5)}$$

Now, $$\log_e \frac{p}{p_1} = -\log \frac{p_1}{p} = -\log\left(1 - \frac{p - p_1}{p}\right)$$

$$= -\left(-\frac{p - p_1}{p}\right) = \frac{p - p_1}{p}$$

[Remembering that $-\log(1 - x) = x$, when x is small quantity]

So, equation (5) can be written as,

$$\frac{p - p_1}{p} = \frac{L_f}{R} \cdot \frac{\Delta T}{T^2} \quad \text{... (6)}$$

From equation (6), it is clear that ***lowering of vapour pressure*** $(p - p_1)$ ***is proportional to depression of freezing point*** (ΔT). As lowering of vapour pressure is also proportional to osmotic pressure, we can say that ***depression of freezing point is also proportional to osmotic pressure.***

For dilute solution, Raoult's law is given by

$$\frac{p - p_1}{p} = \frac{n_1}{n_2}$$

where, n_1 and n_2 are the number of moles of the solute and solvent, respectively. So,

$$\frac{L_f}{R} \cdot \frac{\Delta T}{T^2} = \frac{n_1}{n_2}$$

or
$$\Delta T = \frac{n_1}{n_2} \cdot \frac{RT^2}{L_f}$$

If w_1 g of a solute of molecular weight m_1 is dissolved in w_2 g of solvent of molecular weight m_2, then $n_1 = w_1/m_1$ and $n_2 = w_2/m_2$.

Therefore, $\dfrac{w_1/m_1}{w_2/m_2} \cdot \dfrac{RT^2}{L_f} = \dfrac{w_1 m_2}{w_2 m_1} \cdot \dfrac{RT^2}{L_f}$

If l_f is the latent heat of fusion per gram of solvent, then $l_f = \dfrac{L_f}{m_2}$. So,

$$\Delta T = \frac{w_1}{w_2 m_1} \cdot \frac{RT^2}{l_f} \qquad \text{... (7)}$$

For a given solvent at its freezing point, T and l_f are constants, so from equation (7),

$$\Delta T = \text{constant} \times \frac{w_1}{w_2 m_1} = \frac{k w_1}{w_2 m_1} \qquad \text{... (8)}$$

where k is a constant known as *depression constant.* If $\dfrac{w_1}{m_1} = 1$, $w_2 = 1$ g then $k = \Delta T$. So, depression constant is defined as the ***depression of freezing point produced by dissolving 1 mole of a solute in 1 g of the solvent.***

If $\dfrac{w_1}{m_1} = 1$ and $w_2 = 100$ g, then from equation (8),

$$\Delta T = \frac{k}{100} = K_{100} \text{ or } K$$

where K (or K_{100}) is also a constant and is known as *molecular depression constant.* So, K (or K_{100}) is defined as the ***'depression of freezing point produced by dissolving 1 mole of a solute in 100 g of the solvent'.*** Therefore, from equation (8)

$$\Delta T = \frac{100\,Kw_1}{w_2 m_1} \qquad \dots (9)$$

If $\frac{w_1}{m_1} = 1$ and $w_2 = 1000\,g$, then from equation (8),

$$\Delta T = \frac{k}{100} = K_{1000} \text{ or } K_f$$

So, K_f (or K_{1000}) is known as *molal depression constant* or *cryoscopic constant.* So, K_f (or K_{1000}) is defined as the ***depression of freezing point produced by dissolving 1 mole of a solute in 1000 g of the solvent.*** Therefore, from equation (8)

$$\Delta T = \frac{1000\,K_f w_1}{w_2 m_1} \qquad \dots (10)$$

Equations (8), (9) and (10) give the relations between depression of freezing point and molecular weight of solute.

Problem 18. ***Explain what is meant by molal depression constant of solvent ? How it is related to latent heat of fusion? Describe a method for determining the molecular weight of a substance by depression in freezing point. Can you determine the normal molecular weight of sodium chloride by this method? If not, explain why?***

[I] Molal Depression Constant (K_f)

It is defined as the *'depression in freezing point produced by dissolving 1 mole of a solute in 1000 g or 1 kg of solvent.'* For example, K_f of water is 1.86°, which means that when 1 mole of any solute is dissolved in 1000 g of water, the depression in freezing point is 1.86°.

[II] Relation Between Molal Depression Constant (K_f) and Latent Heat of Fusion (L_f)

vant' Hoff showed that by thermodynamic reasoning, we can obtain the following expression :

$$K_f^* = \frac{RT^2}{1000L_f}$$

where, T = freezing point of the solvent on the absolute scale, R = gas constant, L_f = latent heat of fusion per gram of solvent. As R = 2 calories,

$$K_f = \frac{0.002\,T^2}{L_f}$$

[III] Determination of Molecular Weight of Non-Volatile Substance

Though a number of methods., *e.g.*, Rast's camphor method, Beckman's method etc. are available for determining the molecular weight of a non-volatile solute, the most convenient method generally and widely employed in the laboratory is *Beckmann's method.*

The apparatus as shown in figure (17) consists of an inner freezing point tube fitted with a Beckmann thermometer (it can read upto 0.01°) and a stirrer. This tube is fitted with a side tube (T) for introducing the solute. The freezing point tube is surrounded by an outer glass tube which serves as an air jacket and ensures a slow and uniform rate of cooling of liquid in the inner tube. The whole apparatus is enclosed in a glass jar containing freezing mixture and is provided with a stirrer.

In the actual experiment, 20g of the pure solvent (water) is taken in the inner freezing tube and stirred gently. The movement of the mercury thread in Beckmann thermometer is watched carefully. The temperature first falls below the freezing point of the solvent. It is then stirred and as the solvent

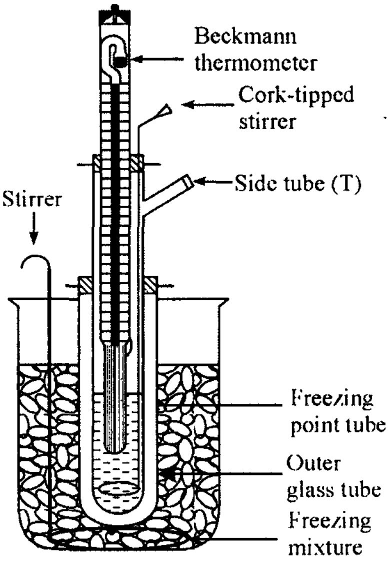

Fig. 17. Beckmann apparatus.

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* For water : L_f = 80 calories and $T = 0 + 273 = 273$ K

Therefore, $K_f = \frac{0.002 \times 273 \times 273}{80} = 1.86°$

starts solidifying, the temperature rises rapidly and finally becomes stationary. This temperature is noted. Let it be T°.

The freezing point tube is taken out of the freezing mixture and the solvent is melted. A weighed amount of the solute (w_1), whose molecular weight is to be determined is then added through the side tube. The experiment is repeated as before and freezing point of the solution is noted. Let it be T_1^*. The depression in freezing point (ΔT) will then be $(T - T_1)^*$.

The molecular weight (m_1) of the non-volatile solute is then calculated from the expression :

$$\Delta T = \frac{1000 K_f w_1}{w_2 m_1}$$

or
$$m_1 = \frac{1000\, K_f w_1}{w_2 \,.\, \Delta T}$$

Knowing all the values of right hand side, we can easily calculate m_1.

[IV] Molecular Weight of Sodium Chloride

The molecular weight of sodium chloride cannot be determined by the above method. The reason is that sodium chloride is an electrolyte and so it dissociates in solution giving greater number of particles of the solute than if it were not dissociated. As the depression in freezing point is proportional to the number of molecules of the solute, the results are thus ***abnormal***, *i.e.*, the observed molecular weight is not equal to the normal molecular weight (58.5) and the former is always less than 58.5.

NUMERICAL PROBLEMS

Ex. 1. ***Calculate the molal depression constant of water, if the latent heat of fusion of ice at 0°C = 80 cal/g.***

Sol. Latent heat of fusion (L_f) = 80.0 cal/g

Freezing point of water (T) = 0°C = 0 + 273 = 273 K

$$\therefore \qquad K_f = \frac{RT^2}{1000 L_f} = \frac{2 \times (273)^2}{1000 \times 80} = \mathbf{1.863^{\circ}}$$

Ex. 2. ***An aqueous solution containing 3.33 g of urea per 250 g of water freezes at − 0.413°C. Calculate the molal depression constant of water.***

Sol. $w_1 = 3.33$; $w_2 = 250$; $\Delta T = 0 - (-\,0.413^{\circ}) = 0.413$; m_1 of urea $= 60$; $K_{1000} = ?$

Now, $$K_{1000} = \frac{w_2 \, . \, m_1 \, . \, \Delta T}{1000 w_2} = \frac{250 \times 60 \times 0.413}{1000 \times 3.33} = \mathbf{1.86^\circ}$$

Ex. 3. ***1.55 g of a substance dissolved in 40 g of benzene lowered the freezing point of benzene by 0.55°C. Calculate the molecular weight of the substance (K_f for benzene is 5.22° per 1000 g).***

Sol. $w_1 = 1.55$; $w_2 = 40$; $\Delta T = 0.55$; $m_1 = ?$

Now, $$m_1 = \frac{1000 K_f \, . \, w_1}{w_2 \Delta T} = \frac{1000 \times 5.22 \times 1.55}{40 \times 0.55} = \mathbf{367.7}$$

Ex. 4. ***1.355 g of a substance dissolved in 55 g of acetic acid produced a depression of 0.618°C in the freezing point. Calculate the molecular weight of the dissolved substance. The molecular depression constant of acetic acid is 3.85° per 1000 g.***

Sol. $w_1 = 1.355$; $w_2 = 55$; $\Delta T = 0.618^\circ$; $K_{1000} = 3.85^\circ$; $m_1 = ?$

Now, $$m_1 = \frac{1000 \times 3.85 \times 1.355}{55 \times 0.618} = \mathbf{153.4}$$

Ex. 5. ***How many grams of methyl alcohol must be added to 10 litre tank of water to prevent its freezing at − 5°C? The molal freezing point constant for water is 1.86°.***

Sol. Let w_1 g of methyl alcohol be added. Then; $w_1 = ?$; $w_2 = 10{,}000$ c.c. $= 10{,}000\,g$; $\Delta T = 0 - (-5) = 5^\circ$; $K_f = 1.86^\circ$; m_1 (of CH_3OH) $= 12 + 3 + 16 + 1 = 32$.

Now, $$w_1 = \frac{w_2 \, . \, m_1 \, . \, \Delta T}{1000 K_f} = \frac{10{,}000 \times 32 \times 5}{1000 \times 1.86} = \mathbf{860.21\ g}$$

Ex. 6. ***The osmotic pressure of a solution containing 1 g mole cane sugar is 5 atmospheres at 50°C. Calculate the freezing point, assuming the solution to be dilute. The latent heat of fusion of water is 80 cal/g.***

Sol. From the first part of the question, we will calculate the value of V, *i.e.*, volume of solution, from the equation :

$$PV = nRT$$

or $$V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 323}{5} = 5.30 \text{ litre}$$

Since the solution is dilute, its density is approximately equal to unity, hence the weight of the solution = 5300 g. Now, we know that,

$$K = \frac{RT^2}{100L_f} = \frac{2 \times (323)^2}{100 \times 80} = 18.6^\circ$$

We also know that,

$$\Delta T = \frac{100Kw_1}{w_2 m_1}$$

Since 1 g mole of cane sugar is dissolved, $w_1 =$ molecular weight = 342.

$$\therefore \qquad \Delta T = \frac{100 \times 18.6 \times 342}{5300 \times 342} = 0.35^\circ$$

∴ Freezing point of solution

= F. pt. of water − ΔT = 0 − 0.35 = **− 0.35°C**

Ex. 7. ***The freezing point of a solution of 0.3210 g naphthalene in 52.12 g of benzene is 5.15°, whereas the freezing point of pure solvent is 5.40°. If the molecular depression per 1000 g of solvent is 5.12°, find the molecular weight of naphthalene.***

Sol. $w_1 = 0.3210$; $w_2 = 52.12$; $K_f = 5.12$;

$\Delta T = 5.40 - 5.15 = 0.25^\circ$; $m_1 = ?$

$$\therefore \qquad m_1 = \frac{1000K_f w_1}{w_2 \,.\, \Delta T} = \frac{1000 \times 5.12 \times 0.3210}{52.12 \times 0.25} = \mathbf{126.13}$$

Ex. 8. ***15 g of a substance dissolved in 150 g of water lowered its freezing point by 1.2° C. Find out the molecular weight of the substance. The molal depression constant for water is 1.85° (1000 g).***

Sol. We have,

$$m = \frac{1000K_f w_1}{w_2 \,.\, \Delta T}$$

Here, $K_f = 1.85$; $w_1 = 15$; $w_2 = 150$; $\Delta T = 1.2$

$$\therefore \qquad m_1 = \frac{1000 \times 1.85 \times 15}{150 \times 1.2} = \mathbf{154.16}$$

Ex. 9. ***The freezing point of pure benzene is 5.4°C and that of a solution containing 2.0 g of a solute per 100 g of benzene is 4.40°C. Calculate the molecular weight of solute (K_{1000} for benzene = 5°).***

Sol. We have,

$$m_1 = \frac{1000 K_f w_1}{w_2 \,.\, \Delta T}$$

Here, $K_f = 5$; $w_1 = 2$; $w_2 = 100$; $\Delta T = 5.4 - 4.4 = 1$

$$\therefore \qquad m_1 = \frac{1000 \times 5 \times 2}{100 \times 1} = \mathbf{100}$$

Ex. 10. ***Calculate the freezing point of the solution produced by dissolving 3.42 g of cane sugar of molecular weight 342 in 50 g of water. Latent heat of fusion of ice is 79.6 cal/g.***

Sol. Freezing point of water (T) = 0°C = 0 + 273 = 273 K

Latent heat of fusion (L_f) = 79.6 cal/g

$$\therefore \qquad K_f = \frac{RT^2}{1000 L_f} = \frac{2 \times (273)^2}{1000 \times 79.6} = 1.872^\circ$$

Also, $w_1 = 3.42$; $w_2 = 50$; $m_1 = 342$; $\Delta T = ?$

$$\therefore \qquad \Delta T = \frac{1000 K_f w_1}{w_2 . m_1} = \frac{1000 \times 1.872 \times 3.42}{50 \times 342} = 0.374^\circ$$

$\therefore$ Freezing point of solution = Freezing point of water $- \Delta T$

$= 0 - 0.374 = -$ **0.374°C**

Ex. 11. ***On dissolving 0.8021 g of hydroxy benzaldehyde ($C_7H_6O_2$) in 20 g of naphthalene (f. pt. = 80.1°C) the freezing point depression was found to be 0.232°C. Find out the molal depression, constant and the latent heat of fusion per gram for naphthalene.***

Sol. Molecular weight of $C_7H_6O_2 = 7 \times 12 + 6 \times 1 + 2 \times 16$ = 122.

We have, $w_1 = 0.8021$; $w_2 = 20$; $m_1 = 122$; $\Delta T = 0.232$; $K_f = ?$

$$\therefore \qquad K_f = \frac{w_2 \,.\, m_1 \,.\, \Delta T}{1000 \,.\, m_1} = \frac{20 \times 122 \times 0.232}{1000 \times 0.8021} = 0.705$$

$$\therefore \qquad K_f = \frac{w_2 \,.\, m_1 \,.\, \Delta T}{1000 \,.\, m_1} = \frac{20 \times 122 \times 0.232}{1000 \times 0.8021} = 0.705$$

We know that, $K_f = \dfrac{RT^2}{1000 L_f}$ ... (1)

$T - 80.1 + 273 = 353.1$ K; $L_f = ?$

$$\therefore \qquad L_f = \frac{RT^2}{1000 K_f} = \frac{2 \times (353.1)^2}{1000 \times 0.705} = \mathbf{353.7\ cal/g} \qquad \text{[From Eq. (1)]}$$

Ex. 12. ***The addition of 4 g of a substance X in 100 g of a solvent S raised the B.P. of S by 0.60 K. Calculate :***

(a) Freezing point depression of S.

(b) Relative vapour pressure lowering of S.

(c) Osmotic pressure of the solution at 300 K.

(d) Molecular mass of X.

(where, K_b and K_f of the solvent are 5.0 and 32.0 respectively, mol. mass of S = 150 and density of the solution is 1.6×10^3 kg mol^{-3}).

Sol.

(a)
$$\Delta T_b = \frac{1000 K_b w_1}{w_2 m_1}$$

or
$$0.60 = \frac{1000 \times 5 \times 4}{100 \times m_1}$$

or
$$m_1 = \frac{1000 \times 5 \times 4}{100 \times 0.6} = 333.33$$

$\therefore$
$$\Delta T_f = \frac{1000 K_f w_1}{w_2 m_1} = \frac{1000 \times 32 \times 4}{100 \times 333.33} = 3..84^\circ$$

$\therefore$ Freezing point depression = **3.84°**.

(b) Relative lowering of V.P.

$$= \frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1} = \frac{4 \times 150}{100 \times 333.33} = \mathbf{0.018}$$

(c) Osmotic pressure,

$\because$
$$P = \frac{\omega}{mV} RT$$

$$P = \frac{4 \times 0.0821 \times 300}{333.33 \times \left(\dfrac{100 \times 1000}{1.6 \times 10^3} \right)} \qquad \left(\because \quad V = \frac{M}{d} \right)$$

$$= \mathbf{0{\cdot}0047\ atm.}$$

(d) The molecular mass of X, as calculated in part (a) = **333.33**.

Problem 19. ***Write short notes on the following :***

(i) Abnormal molecular weights or abnormal solutes. **(Meerut 2007)**

(ii) van't Hoff factor. **(Meerut 2005)**

(iii) Abnormal osmotic pressure.

(iv) Degree of association.

(v) Beckmann thermometer.

(vi) Osmotic coefficient.

(1) Abnormal Molecular Weights or Abnormal Solutes

It is seen that the molecular weights of certain substances, *e.g.*, NaCl, KNO_3 etc. in water when determined by any of the methods such as, osmotic pressure, lowering of vapour pressure, elevation in boiling point, depression in freezing point, are less than their normal molecular weights. However, molecular weights of certain substances (like benzoic acid in benzene) are greater than their normal molecular weights. The reason for this anomaly is that the substances either dissociate or associate in solution. The molecular weights thus obtained are far from normal. These are molecular weights known as ***abnormal molecular weights.*** Those solutes which give abnormal molecular weight are known as ***abnormal solutes***. This fact is explained as follows :

We know that the osmotic pressure (P) is directly proportional to concentration (C), which in turn is proportional to the number of particles. It is also established that the osmotic pressure is directly proportional to lowering of vapour pressure (Δp) and the latter is proportional to elevation of boiling point and depression in freezing point (ΔT). All these properties are in turn inversely proportional to molecular weight of the substance. Mathematically,

$$P \propto C \propto \text{No. of particles} \propto \Delta p \propto \Delta T \propto \frac{1}{\text{Mol. wt.}}$$

i.e.,

$$\text{Mol. wt} \propto \frac{1}{\text{Number of particles}}$$

In dissociation, the number of particles increases and so the observed molecular weight is less than the normal molecular weight. In association, the number of particles decreases and thus, the observed molecular weight is higher than the normal molecular weight. Thus,

$$\text{Normal mol. wt} \propto \frac{1}{\text{Normal number of particles}}$$

$$\text{Observed mol. wt.} \propto \frac{1}{\text{Number of particles after dissociation or association}}$$

$$\therefore \quad \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{No. of particles after dissociation or association}}{\text{Normal number of particles}}$$

(2) van't Hoff Factor

van't Hoff showed that all properties, *e.g.*, osmotic pressure (P), lowering of vapour pressure (Δp), elevation in boiling point (ΔT), depression in freezing point (ΔT) depend upon the concentration (C) of the solute, *i.e.*, on the number of particles of solute. These properties are known as ***colligative properties.****
For electrolytes, the number of particles increases and so the above colligative properties are all higher for solutions of electrolytes than for non-electrolytes of the same molecular concentration. The above colligative properties have a lower value for solutes which associate in solution. To account for this, van't Hoff introduced a factor known as vant Hoff factor (i). It is represented by,

$$i = \frac{P_{obs}}{P_{nor}} = \frac{\Delta p_{obs}}{\Delta p_{nor}} = \frac{\Delta T_{obs}}{\Delta T_{nor}}.$$

In general, $i = \dfrac{\text{Observed colligative property of an electrolyte}}{\text{Normal colligative property of an electrolyte}}$

Since these properties vary inversely as molecular weight of solutes, it follows that, van't Hoff factor,

$$i = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

(3) Degree of Association

It is defined as the, *fraction of the total number of molecules which associate or combine to form bigger molecules.*

Consider one mole of a solute X in a given volume of a solvent. Let n simple molecules of X combine to give an associated molecule as follows :

$$nX \rightleftharpoons (X)_n$$

Let x be the degree of association. Thus,

Number of molecules before association $= 1$
Number of unassociated molecules $= 1 - x$
Number of associated molecules $= x/n$

$\therefore$ Total number of effective molecules $= 1 - x + \dfrac{x}{n}$

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* Colligative property of a substance is that property which depends only on the number of particles in solution.

We know that :

$$\frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{No. of molecules after association}}{\text{No. of molecules before association}}$$

or
$$\frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{1 - x + (x/n)}{1}$$

Knowing the value of n, *i.e.*, number of simple molecules which combine to give one associated molecule, x the degree of association can be easily calculated*.

(4) Abnormal Osmotic Pressure

When the osmotic pressure of substances other than non-electrolytes are measured, the values are either much higher or lower than those calculated from the general solution equation $PV = nRT$. It is due to the fact that in such cases, the molecules either dissociate or associate in solutions and since the osmotic pressure is directly proportional to the concentration, *i.e.*, number of particles in solution, the osmotic pressure will thus be either higher or lower than the normal value. The observed osmotic pressure will be higher for substances which dissociate in solution than those substances, which neither dissociate nor associate. The observed osmotic pressure values are thus known as ***abnormal osmotic pressures.***

The ratio of observed osmotic pressure and normal osmotic pressure is called the van't Hoff factor, i. Thus,

$$i = \frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}} = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

$$\left(\text{As O.P.} \propto \frac{1}{\text{Mol. Wt.}}\right)$$

(5) Beckmann Thermometer

Beckmann thermometer is a very sensitive thermometer. It is graduated in one hundredths (1/100) of a degree over a range of

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* Benzoic acid in benzene associates as double molecules, *i.e.*, $n = 2$. Thus,

$$\underset{\substack{1\\(1-x)}}{2C_6H_5COOH} = \underset{\substack{0\\x/2}}{(C_6H_5COOH)_2}$$

$$\frac{\text{Normal mol. wt.}}{\text{Observed mol. wt}} = \frac{\text{No. of molecules after association}}{\text{No. of molecules before association}}$$

$$= \frac{1 - x + (x/2)}{1} = \frac{1 - (x/2)}{1}$$

Thus, x can be easily calculated.

0–6 degrees. It has one large bulb at the bottom of a fine capillary tube. There is a small mercury reservoir at the top. The amount of mercury in this reservoir can be increased or decreased by gently tapping the top of the thermometer. Thus, the thermometer is adjusted so that the top of the mercury thread may rest at any desired point on the scale, when the thermometer is placed in the boiling or freezing solvent. This thermometer is very helpful for measuring small differences of temperature accurately. It is thus also known as a *differential thermometer.*

(6) Osmotic Coefficient

The ratio of van't Hoff factor (i) and the number of ions (n) produced by 1 molecule of a solute is known as *osmotic coefficient.* It is represented by g. In other words, the ratio of observed osmotic pressure and osmotic pressure after complete dissociation is also known as *osmotic coefficient.* Thus,

$$g = \frac{\text{Observed osmotic pressure after dissociation}}{\text{Osmotic pressure after complete dissociation}}$$

$$g = \frac{i}{n}$$

The observed osmotic coefficient is always less than unity. Therefore, $(1 - g)$ is a measure of both inter-ionic attraction and partial dissociation. For those electrolytes which are not completely ionised and exert inter-ionic attraction, the value of g is less than unity.

Problem 20. ***Explain the following statements :***

(i) M/10 solution of NaCl and glucose though equimolar are not isotonic. **(Meerut 2005)**

(ii) The boiling point of solvent is elevated and its freezing point depressed by the addition of a solute.

(i) Isotonic solutions are those solutions which exert the same osmotic pressures. This is true for those solutes which do not dissociate in solution. In such a case, the number of particles before and after dissociation remain the same and so observed and normal osmotic pressures remain the same.

M/10 solutions of NaCl and glucose are no doubt equimolar, but NaCl is an electrolyte, while cane sugar is not. So, NaCl will dissociate giving rise to larger number of particles and so observed osmotic pressure will be more than glucose, which do not dissociate. So, the two solutions will not be isotonic.

(ii) When a liquid is heated, its vapour pressure rises and when it equals the atmospheric pressure, the liquid boils. When non-volatile solute is added to the liquid, it lowers the vapour pressure. Therefore, it elevates the boiling point as the solution has to be heated to a higher temperature to make its vapour pressure become equal to the atmospheric pressure.

Freezing point is the temperature at which the solid and liquid states of a substance have the same vapour pressure. As the vapour pressure of a solution is invariably less than that of the solvent, the solution freezes at a temperature lower than that of pure solvent. Thus, there is a depression in freezing point of the solvent on the addition of a solute to it.

NUMERICAL PROBLEMS BASED ON DISSOCIATION, ASSOCIATION AND VAN'T HOFF FACTOR

[I] Osmotic Pressure

Ex. 1. ***Calculate the osmotic pressure of 20% anhydrous $CaCl_2$ solution of 0°C assuming the salt to be completely ionised.*** **(*Ca* = 40, *Cl* = 35.5).**

Sol. The normal osmotic pressure of $CaCl_2$ is given by,

$$P_{nor} = \frac{w}{mV} \cdot RT = \frac{20}{111 \times 0.1} \times 0.0821 \times 273$$
$$= 40.38 \text{ atmosphere.}$$

[Mol. wt. of $CaCl_2 = 40 + 2 \times 35.5 = 111$]

If $CaCl_2$ is completely ionised, one mole of it gives 3 particles. *i.e.*,

$$\begin{array}{cccccl} CaCl_2 & \rightleftharpoons & Ca^{++} & + & 2Cl^- & \\ 1 & & 0 & & 0^- & \text{(Before dissociation)} \\ 0 & & 1 & & 2 & \text{(After complete dissociation)} \end{array}$$

No. of particles before dissociation = 1

No. of particles after dissociation = 3.

Now, $$\frac{\text{O.P. (observed)}}{\text{O.P. (normal)}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\text{O.P. (observed)} = \frac{3}{1} \times 40.38 = \mathbf{121.14 \text{ atmospheres}}$$

Ex. 2. ***A 1% solution of KCl is dissociated to an extent of 80%. What would be its osmotic pressure at 27°C?***

Sol. Molecular weight of KCl = 39 + 35.5 = 74.5

As before, the normal O.P. is calculated as follows, *i.e.*,

$$P = \frac{w}{mV} \cdot RT = \frac{1}{74.5 \times 0.1} \times 0.0821 \times 300$$
$$= 3.306 \text{ atmospheres.}$$

Potassium chloride dissociates as follows :

$$\begin{array}{llll} KCl \rightleftharpoons & K^+ & + \; Cl^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1 - 0.80 & 0.80 & 0.80 & \text{(After dissociation)} \end{array}$$

No. of particles before dissociation = 1

No. of particles after dissociation = 1 − 0.80 + 0.80 + 0.80
= 1.80

Now, $$\frac{\text{O.P. (observed)}}{\text{O.P. (normal)}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\text{O.P. (observed)} = \frac{1.80}{1} \times 3.306 = \mathbf{5.95\ atm.}$$

Ex. 3. ***Calculate the osmotic pressure of N/10 NaCl solution which ionises to an extent of 80% at 27°C.***

Sol. Normal molecular weight of NaCl = 23 + 35.5 = 58.5

Normal osmotic pressure can be calculated as follows :

$$P = \frac{w}{mV} RT$$

N/10 solution of NaCl means 5.85 g of NaCl is dissolved in 1 litre. Therefore, $w = 5.85$; $V = 1$; $m = 58.5$; $T = 27 + 273 = 300$ K.

$$\therefore \qquad P = \frac{5.85 \times 0.0821 \times 300}{58.5 \times 1} = 2.463 \text{ atm.}$$

The degree of dissociation NaCl is represented as :

$$\begin{array}{llll} NaCl \rightleftharpoons & Na^+ & + \; Cl & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1 - \alpha & \alpha & \alpha & \text{(After dissociation)} \end{array}$$

where, α = degree of dissociation = 0.8

Now, $$\frac{\text{O.P. (observed)}}{\text{O.P. (normal)}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\frac{\text{O.P. (observed)}}{2.463} = \frac{1 - \alpha + \alpha + \alpha}{1} = \frac{1 + \alpha}{1} = \frac{1 + 0.8}{1} = \frac{1.8}{1}$$

or $$\text{Observed O.P.} = 2.463 \times 1.8 = \mathbf{4.433\ atm.}$$

Ex. 4. ***The osmotic pressure of a 0.5N solution of NaCl is 20.29 atmospheres at 18°C. Calculate the degree of dissociation of the salt.***

Sol. Observed O.P. = 20.29 atmospheres.

The normal O.P. can be calculated from the formula by putting the molecular weight of NaCl = 23 + 35.5 = 58.5.

0.5N solution of NaCl means that 0.5 × 58.5, *i.e.*, 29.25 g of NaCl is dissolved in 1 litre, so that

$$w = 29.25;\ V = 1;\ m = 58.5;\ T = 273 + 18 = 291 \text{ K}$$

Therefore, $P = \frac{w}{mV} \cdot RT = \frac{29.25 \times 0.0821 \times 291}{58.5 \times 1} = 11.94$ atm.

NaCl dissociates as follows :

$$\begin{array}{llll} NaCl \rightleftharpoons & Na^+ + & Cl^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & \alpha & \alpha & \text{(After dissociation)} \end{array}$$

where, α = degree of dissociation = 0.8

Now, $$\frac{\text{O.P. (observed)}}{\text{O.P. (normal)}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\frac{20.29}{11.94} = \frac{1-\alpha+\alpha+\alpha}{1} = \frac{1+\alpha}{1} = 1+\alpha$$

or $$\alpha = \frac{20.29 - 11.94}{11.94} = \frac{8.35}{11.94} = 0.6993$$

∴ Degree of dissociation = **69.93%**

Ex. 5. ***Find out the osmotic pressure of a decinormal solution of NaCl at 27°C, taking NaCl to be 40% dissociated at this dilution.*** **(Meerut 2006)**

Sol. The molecular weight of NaCl = 58.5

The normal O.P. can be calculated from the relation

$$P = \frac{w}{mV} \cdot RT$$

N/10 NaCl solution means that 58.5/10, *i.e.*, 5.85 g of NaCl are dissolved in 1 litre. Thus,

$$P = \frac{5.85 \times 0.0821 \times 300}{58.5 \times 1} = \textbf{2.463 atmospheres}$$

The dissociation of NaCl is as follows :

$$\begin{array}{llll} NaCl \rightleftharpoons & Na^+ + & Cl^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1-0.4 & 0.4 & 0.4 & \text{(After dissociation)} \end{array}$$

∴ $$\frac{\text{O.P. (observed)}}{\text{O.P. (normal)}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\text{O.P. (observed)} = \frac{1-0.4+0.4+0.4}{1} \times 2.463$$

or $= 1.4 \times 2.463 = \mathbf{3.4482}$ **atmospheres.**

Ex. 6. ***A 3.4% solution of $BaCl_2$ is isotonic with a 7.2% solution of glucose ($C_6H_{12}O_6$). Calculate the degree of dissociation and the van't Hoff factor for $BaCl_2$ solution.*** **($Ba = 137.3, H = 1, C = 12, O = 16, Cl = 35.5$).**

Sol. Since the solutions are isotonic, we have

$$\underset{BaCl_2}{\frac{w_1}{m_1V_1}} = \underset{\text{Glucose}}{\frac{w_2}{m_2V_2}}$$

$$\frac{3.4}{m_1 \times 0.1} = \frac{7.2}{180 \times 0.1}$$

or
$$m_1 = \frac{180 \times 0.1 \times 3.4}{72 \times 0.1} = 85$$

This molecular weight is the observed or experimental molecular weight of $BaCl_2$.

The normal molecular weight of $BaCl_2 = 137.3 + 71 = 208.3$

$BaCl_2$ dissociates as follows :

$$\begin{array}{cccl} BaCl_2 \rightleftharpoons & Ba^{++} & + \; 2Cl^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & \alpha & 2\alpha & \text{(After dissociation)} \end{array}$$

where, $\alpha =$ degree of dissociation.

Now, $$\frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or
$$\frac{85}{208.3} = \frac{1}{1-\alpha+\alpha+2\alpha} \quad \text{or} \quad \frac{85}{208.3} = \frac{1}{1+2\alpha}$$

or
$$2\alpha = \frac{208.3}{2} - 1 = 2.45 - 1 = 1.45$$

or
$$\alpha = \frac{1.45}{2} = 0.725$$

$\therefore$ Degree of dissociation = **72.5%.**

$$\text{van't Hoff factor} = \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{208.3}{85} = \mathbf{2.45}$$

Ex. 7. ***If a solution of mercuric cyanide containing 3 g per litre has an osmotic pressure of 232 mm at 25°C, what is the apparent molecular weight and the degree of dissociation of mercuric cyanide?*** **($Hg = 200.6, C = 12, N = 14$).**

Sol. Normal molecular weight of

$$Hg(CN)_2 = 200.6 + 2\,(12 + 14) = 252.6$$

Experimental or observed molecular weight can be calculated from the given data and according to the equation,

$$P = \frac{w}{mV} \cdot RT$$

$$m = \frac{w \cdot RT}{PV} = \frac{3 \times 0.0821 \times 298}{\frac{238}{760} \times 1} = 234.37$$

Mercuric cyanide dissociates as follows :

$$\begin{array}{cccccl} Hg(CN)_2 & \rightleftharpoons & Hg^{++} & + & 2CN^- & \\ 1 & & 0 & & 0 & \text{(Before dissociation)} \\ 1-\alpha & & \alpha & & 2\,\alpha & \text{(After dissociation)} \end{array}$$

Now, $\dfrac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \dfrac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$

or $$\frac{234.37}{252.6} = \frac{1}{1 + 2\,\alpha}$$

or $$\alpha = 0.0389$$

(i) Apparent or observed molecular weight = **234.37**

(ii) Degree of dissociation = **3.89%**

[II] Lowering of Vapour Pressure

Ex. 8. ***At 0°C, vapour pressure of water = 4.62 mm and that of 2.28 g of $CaCl_2$ in 100 g of water = 4.584 mm. Calculate the degree of dissociation of the salt.***

Sol. Normal molecular weight of $CaCl_2 = 40 + 71 = 111$.

Observed molecular weight of $CaCl_2$ can be calculated from the given data and using the equation,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or $$\frac{4.62 - 4.584}{4.62} = \frac{28 \times 18}{100 \times m_1}$$

or $$m_1 = \frac{4.62 \times 2.28 \times 18}{100 \times 0.036} = 52.668$$

The dissociation of $CaCl_2$ is as follows :

$$\begin{array}{cccccl} CaCl_2 & \rightleftharpoons & Ca^{++} & + & 2Cl^- & \\ 1 & & 0 & & 0 & \text{(Before dissociation)} \\ 1-\alpha & & \alpha & & 2\,\alpha & \text{(After dissociation)} \end{array}$$

Now, $$\frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

or $$\frac{52.668}{111} = \frac{1}{1+2\alpha}$$

or $$2\alpha = \frac{111}{52.668} - 2 = 2.107 - 1 = 1.107$$

or $$\alpha = \frac{1.107}{2} = 0.5535$$

∴ Degree of dissociation = **55.35%**

Ex. 9. ***A 2.85% aqueous solution of sodium nitrate was found to have a vapour pressure of 751 mm at 100°C. Calculate the degree of dissociation of the salt at this dilution.***

Sol. The vapour pressure (p) of pure solvent at 100° = 760 mm.

Therefore, the observed molecular weight (m_1) can be calculated as follows :

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or $$\frac{760 - 751}{760} = \frac{2.85 \times 18}{100 \times m_1} \qquad \text{[Molecular weight of } H_2O = 18]$$

or $$m_1 = \frac{2.85 \times 18 \times 760}{100 \times 9} = 43.32$$

The theoretical molecular weight of $NaNO_3$ = 23 + 14 + 48 = 85

$NaNO_3$ dissociates as follows :

$$\begin{array}{cccl} NaNO_3 & \rightleftharpoons Na^+ & + \; NO_3^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & \alpha & \alpha & \text{(After dissociation)} \end{array}$$

Now, $$\frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

or $$\frac{43.32}{85} = \frac{1}{1+\alpha}$$

or $$\alpha = \frac{85}{43.32} - 1 = 1.962 - 1 = \mathbf{0.962}$$

∴ Degree of dissociation = **96.2%**

Ex. 10. ***A solution containing 4.81 g of mercuric cyanide in 100 g of water has a vapour pressure of 755.2 mm at 100°C. What is the apparent molecular weight, degree of dissociation and van't Hoff factor of the salt?***

Sol. The observed molecular weight (m_1) of $Hg(CN)_2$ can be calculated from the equation,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

$$\therefore \quad \frac{760 - 755.2}{76} = \frac{4.81 \times 18}{100 \times m_1}$$

(V.P. of H_2O at 100° = 760 mm; mol. wt. of H_2O = 18)

or $$m_1 = \frac{760 \times 4.81 \times 18}{4.8 \times 100} = 137.08$$

Normal molecular weight of $Hg(CN)_2$ = 252.6

$Hg(CN)_2$ dissociates as follows :

$$\begin{array}{cccl} Hg(CN)_2 & \rightleftharpoons \; Hg^{++} & + \; 2CN^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1 - \alpha & \alpha & 2\alpha & \text{(After dissociation)} \end{array}$$

Now, $$\frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

or $$\frac{137.08}{252.6} = \frac{1}{1 + 2\alpha}$$

or $$2\alpha = \frac{252.6}{137.08} - 1 = 1.842 - 1 = 0.842$$

or $$\alpha = 0.421$$

Now, $$\text{van't Hoff factor} = \frac{\text{Normal mol. wt}}{\text{Observed mol. wt.}}$$

$$= \frac{252.6}{137.08} = 1.842$$

(i) Apparent molecular weight = **137.08**

(ii) Degree of dissociation = **42.1%**

(iii) Van't Hoff factor = **1.842**

[III] Elevation of Boiling Point

Ex. 11. ***A solution of $BaCl_2$ containing 9.0 g of the anhydrous salt per litre boils at 100.056°C under a pressure of 760 mm Hg. Calculate the degree of dissociation of the salt, if the molar elevation constant for water is 0.52° per 1000 g. Also calculate the van't Hoff factor. (Ba = 137.3, Cl = 35.5).***

Sol. The normal molecular weight of

$$BaCl_2 = 137.3 + 71.0 = 208.3$$

The experimental or observed molecular weight (m_1) of $BaCl_2$ can be calculated from the given data.

$w_1 = 9.0$; $w_2 = 1000$; $\Delta T = 100.056 - 100 = 0.056°$; $K_b = 0.52$; $m_1 = ?$

$$\therefore \quad m_1 = \frac{1000 K_b\, w_1}{w_2 \,.\, \Delta T} = \frac{1000 \times 0.52 \times 9}{1000 \times 0.056} = 83.57$$

$BaCl_2$ dissociates as follows :

$$\begin{array}{cccl} BaCl_2 & \rightleftharpoons Ba^{++} & + \; 2Cl^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & \alpha & 2\alpha & \text{(After dissociation)} \end{array}$$

Now, $$\frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

or $$\frac{83.57}{208.3} = \frac{1}{1+2\alpha} \quad \text{or} \quad \alpha = 0.7462\%$$

$\therefore$ Degree of dissociation = **74.62%**

$$\therefore \quad \text{van't Hoff factor} = \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{208.3}{83.57} = \mathbf{2.492}$$

Ex. 12. ***The boiling point of an aqueous solution containing 5 g KCl per litre at 760 mm pressure is 100.065°C. Calculate the degree of dissociation*** **(K_b = 0.54).**

Sol. Normal molecular weight of KCl = 39 + 35.5 = 74.5

Observed molecular weight, m

$$= \frac{1000 K_b}{w_2 \Delta . T} = \frac{100 \times 0.54 \times 5}{1000 \times 0.065} = 41.53$$

KCl dissociates as :

$$\begin{array}{cccl} KCl & \rightleftharpoons K^+ & + \; Cl^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ (1-\alpha) & \alpha & \alpha & \text{(After dissociation)} \end{array}$$

where, α = degree of dissociation.

No. of particles after dissociation $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$\therefore \quad \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\frac{74.5}{41.53} = \frac{1+\alpha}{1}$$

or $$\alpha = \frac{74.5}{41.53} - 1 = 1.793 - 1 = 0.793$$

$\therefore$ Degree of dissociation = **79.3%**

Ex. 13. ***A solution of KCl containing 5 g per litre boils at 100.065°C at 760 mm. Determine the degree of dissociation of KCl and van't Hoff factor. Given that : $K_{1000} = 0.54°$; $K = 39$, $Cl = 35.5$.***

Sol. See Ex. 12.

Ex. 14. ***A solution of barium nitrate containing 11.07 g of the salt in 100 g of water boils at 100.466°. The boiling point of a solution of a normal non-dissociating salt containing 1g mole of a salt in 1000 g of water is 100.52°C. Calculate the degree of dissociation of barium nitrate in the solution. (Mol. wt. of barium nitrate = 261.5).***

Sol. According to definition, molal elevation constant (K_b) is defined as, *"the elevation in b. pt. when 1 g mole of a solute is dissolved in 1000 g of the solvent"*, and thus according to the second sentence of the question, the elevation in b. pt. of a solution containing 1 g mole of the non-dissociating salt is 0.52. Thus, $K_b = 0.52°$.

Now, $w_1 = 11.07, w_2 = 100, \Delta T = 100.466 - 100 = 0.466°$,

$K_b = 0.52, m_1 = ?$

$$\text{Thus, } m_1 = \frac{1000K_b \cdot w_1}{w_2 \Delta T} = \frac{1000 \times 0.52 \times 11.07}{100 \times 0.466} = 123.5$$

$Ba(NO_3)_2$ dissociates as follows :

$$\begin{array}{lcccl} Ba(NO_3)_2 & \rightleftharpoons & Ba^{++} & + \; 2NO_3^- & \\ 1 & & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & & \alpha & 2\alpha & \text{(After dissociation)} \end{array}$$

$$\text{Now, } \frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

$$\text{or} \quad \frac{123.5}{261.5} = \frac{1}{1+2\alpha}$$

$$\text{or} \quad \alpha = 0.5587$$

∴ Degree of dissociation = **55.87%**

Ex. 15. ***Acetic acid associates in benzene to form double molecules. 1.65 g of acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.36°C. Calculate the van't Hoff factor and the degree of association of acetic acid in benzene. Molal elevation constant of benzene is 2.57°.***

Sol. Normal molecular weight of $CH_3COOH = 60$.

Now, $w_1 = 1.65, w_2 = 100, \Delta T = 0.36, K_b = 2.57°, m_1 = ?$

Therefore, $m_1 = \dfrac{1000K_b \cdot w_1}{w_2\,\Delta T} = \dfrac{1000 \times 2.57 \times 1.65}{100 \times 0.36} = 117.79$

van't Hoff factor $= \dfrac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \dfrac{60}{117.79} = \mathbf{0.509}$.

Since acetic forms double molecules on association, therefore, we have

$$\begin{array}{ccc} 2CH_3COOH & \rightleftharpoons & (CH_3COOH)_2 & \\ 1 & & 0 & \text{(Before association)} \\ 1-\alpha & & \alpha/2 & \text{(After association)} \end{array}$$

where α = degree of association.

Now, $\dfrac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \dfrac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$

or $\dfrac{117.79}{60} = \dfrac{1}{1-\alpha+\dfrac{\alpha}{2}}$ or $\dfrac{117.79}{60} = \dfrac{1}{1-\dfrac{\alpha}{2}}$

or $1-\dfrac{\alpha}{2} = \dfrac{60}{117.79}$

∴ Degree of association = **98.14%**

Ex. 16. ***The latent heat of vaporisation of CS_2 is 85.9 cal and its boiling point is 46.2°C. A solution of 0.9380 g benzoic acid in 50.0 g CS_2 boils at 47.380°C. Calculate the apparent molecular weight and van't Hoff factor.***

Sol. Normal mol. wt. of benzoic acid (C_6H_5COOH) = 122.

Value of '*K*' of CS_2 can be calculated from the equation,

$$K_b = \frac{RT^2}{1000L_e} = \frac{2 \times (319.2)^2}{1000 \times 85.9} = 2.372$$

We have, $w_1 = 0.9380$, $w_2 = 50$, $\Delta T = 47.380 - 46.2 = 1.18°$, $m_1 = ?$

Thus, $m_1 = \dfrac{1000K_b w_1}{w_2 \Delta T} = \dfrac{1000 \times 2.372 \times 0.9380}{50 \times 1.18} = 37.71$

∴ (i) Apparent molecular weight = **37.71**

(ii) van't Hoff factor $= \dfrac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \dfrac{122}{37.71} = \mathbf{3.23}$

[IV] Depression of Freezing Point

Ex. 17. ***The solution obtained by dissolving 1.26 g of sodium chloride in 50 g of water freezes at –1.53C. Calculate the degree of dissociation of sodium chloride. K_f for 1000 g of water is 1.86°C.***

Sol. Normal molecular weight of NaCl = 23 + 35.5 = 58.5.

We have, $w_1 = 1.26; w_2 = 50; \Delta T = 0 - (-1.53) = 153; m_1 = ?$ $K_f = 1.86°$.

$$\text{Therefore, } m_1 = \frac{1000K_f w_1}{w_2 \Delta T} = \frac{1000 \times 1.86 \times 1.26}{50 \times 1.53} = 30.63$$

$$\text{Now, } \frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

$$\text{or } \quad \frac{30.63}{58.5} = \frac{1}{1+(2-1)\,\alpha} = \frac{1}{1+\alpha}$$

(As NaCl gives 2 ions on dissociation)

$$\text{or } \quad \alpha = \frac{58.5}{30.63} - 1 = 1.909 - 1 = 0.909$$

∴ Degree of dissociation = **90.9%**

Ex. 18. ***The freezing point of a solution of 4 g of cadmium iodide in 95 c.c. of water is − 0.22°C. Calculate the apparent molecular weight of cadmium iodide and its degree of dissociation. (K_{1000} = 1.85°, Cd = 112 : I = 127).*** **(Meerut 2007)**

Sol. Normal molecular weight of CdI_2

$$= 112 + 2 \times 127 = 366.$$

We have, $w_1 = 4; w_2 = 95; \Delta T = 0 - (-0.22) = 0.22; m_1 = ?$

$$\text{Thus, } \quad m_1 = \frac{1000K_f w_1}{w_2 \Delta T} = \frac{1000 \times 1.85 \times 4}{95 \times 0.22} = 354.06$$

$$\text{Now, } \frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

$$\text{or } \quad \frac{354.06}{366} = \frac{1}{1+2\alpha} \qquad (\text{As } n \text{ for } CdI_2 = 3)$$

$$\text{or } \quad 2\alpha = \frac{366}{354.06} - 1 = 1.033 - 1 = 0.033$$

$$\text{or } \quad \alpha = 0.0165$$

(i) Apparent molecular weight = **354.06**

(ii) Degree of dissociation = **1.65%**

Ex. 19. ***Phenol associates in benzene to a certain extent to form dimer. A solution containing 20×10^{-3} kg of phenol in 1.0 kg of benzene has its freezing point depressed by 0.69Å. Calculate the fraction of phenol that has dimerised. K_f for benzene = 5.12 kg mol^{-1} K.***

Sol The association of phenol occurs as :

$$\begin{array}{ccl} 2C_6H_5OH \rightleftharpoons & (C_6H_5OH)_2 & \\ 1 & 0 & \text{(Before association)} \\ (1-\alpha) & \alpha/2 & \text{(After association)} \end{array}$$

where $\alpha =$ degree of association.

No. of particles after association $= 1 - \alpha + \alpha/2 = 1 - \alpha/2$

No. of particles before association$= 1$

Normal molecular weight of phenol (C_6H_5OH)

$$= 72 + 5 + 16 + 1 \;\; = 94$$

The observed molecular weight (m_1) of phenol can be calculated from the formula,

$$\Delta T = \frac{1000 K_f w_1}{w_2 m_1}$$

or
$$0.69 = \frac{1000 \times 5.12 \times 10 \times 10^{-3}}{1.0 \times m_1}$$

$$m_1 = \frac{1000 \times 5.12 \times 20 \times 10^{-3}}{1.0 \times 0.69} = 148.4$$

$$\frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

$$\frac{148.4}{94} = \frac{1}{1 - \alpha/2}$$

On solving, $\alpha = 0.7332$

$\therefore$ Phenol is **73.32% dimerised.**

Ex. 20. ***Phenol (C_6H_5OH) associates in water to double molecules. When 0.75 g of phenol is dissolved in 45 g of water, the freezing point depressed by 0.255°C. Calculate the degree of association of phenol. (K_f for water is 1.86° per 1000 g).***

Sol. Normal molecular weight of $C_6H_5OH = 72 + 6 + 16 = 94$.

The observed or apparent molecular weight (m_1) can be calculated for which $w_1 = 0.75$; $w_2 = 45$; $T = 0.255$; $m_1 = ?$

$$\text{Hence, } m_1 = \frac{1000 K_f w_1}{w_2 \Delta T} = \frac{1000 \times 1.86 \times 0.75}{45 \times 0.255} = 121.56$$

Phenol associates as follows :

$$\begin{array}{ccl} 2C_6H_5OH \rightleftharpoons & (C_6H_5OH)_2 & \\ 1 & 0 & \text{(Before association)} \\ (1-\alpha) & \alpha/2 & \text{(After association)} \end{array}$$

where, α = degree of association.

$$\text{Now,} \quad \frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

$$\text{or} \quad \frac{121.56}{94} = \frac{1}{1 - \alpha + (\alpha/2)}$$

$$\text{or} \quad \frac{121.56}{94} = \frac{1}{1 - (\alpha/2)}$$

$$\text{or} \quad 1 - \frac{\alpha}{2} = \frac{94}{121.56}$$

$$\text{or} \quad \alpha = 2\left[1 - \frac{94}{121.56}\right] = 0.4536$$

∴ Degree of association = **45.36%**

Ex. 21. ***A solution containing 0.2965 g of benzoic acid in 2027 g benzene freezes at temperature 0.317°C below the freezing point of the solvent. The freezing point of benzene is 5.5°C and its latent heat of fusion is 30.1 cal /g. Calculate the degree of association of benzoic acid, if it forms double molecules.***

Sol. We have,

$$K_f = \frac{RT^2}{1000L_f} = \frac{2 \times (5.5 + 273)^2}{1000 \times 30.1} = \frac{2 \times (278.5)^2}{1000 \times 30.1} = 5.15$$

Normal molecular weight of benzoic acid (C_6H_5COOH) = 122.

We have, $w_1 = 0.2965$; $w_2 = 20.27$; $\Delta T = 0.317$; $m_1 = ?$

$$\text{Thus} \quad m_1 = \frac{1000K_f w_1}{w_2 \Delta T} = \frac{1000 \times 5.15 \times 0.2965}{20.27 \times 0.317} = 237.63$$

Benzoic acid associates as follows :

$$\begin{array}{ccl} 2C_6H_5COOH \rightleftharpoons & (C_6H_5COOH)_2 & \\ 1 & 0 & \text{(Before association)} \\ 1 - \alpha & \alpha/2 & \text{(After association)} \end{array}$$

where, α = degree of association.

$$\text{Now,} \quad \frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before association}}{\text{No. of particles after association}}$$

$$\text{or} \quad 1 - \frac{237.63}{122} = \frac{1}{1 - \alpha + (\alpha/2)} = \frac{1}{1 - (\alpha/2)}$$

$$\text{or} \quad 1 - \frac{\alpha}{2} = \frac{122}{237.63}$$

$$\text{or} \quad \alpha = 0.9732$$

∴ Degree of association = **97.32%**

Ex. 22. ***A 0.5% aqueous solution of potassium chloride is found to freeze at – 0.24°C. Calculate the van't Hoff factor of the solute at this concentration. K_f for water is 1.86° for 1000 g.***

Sol. The observed molecular weight (m_1) of KCl is given by,

$$m_1 = \frac{1000 K_f w_1}{w_2 \Delta T}$$

Here, $w_1 = 0.5$; $w_2 = 100$; $\Delta T = (0 - 0.24) = 0.24$

$$\because \qquad m_1 = \frac{1000 \times 1.86 \times 0.5}{100 \times 0.24} = 38.75$$

Normal molecular weight of KCl = 39 + 35.5 = 74.5.

$$\therefore \qquad \text{van't Hoff factor} = \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{74.5}{38.75} = 1.92$$

$\therefore$ van't Hoff factor = **1.92**

Ex. 23. ***The freezing point of a solution of 1 g of a monobasic acid in 100 g of water was found to be – 0.168°C. 0.200 g of the acid when dissolved and titrated required 15.1 c.c. of N/10 alkali. Calculate the degree of ionisation of the acid in the solution. The molecular depression for 1000 g of water is 1.85°.***

Sol. From the second sentence of the question, we can easily calculate the theoretical molecular weight of the monobasic acid.

15.1 c.c. of N/10 alkali ≡ 0.2 g acid

or 1.51 c.c. of N alkali ≡ 0.2 g acid

or $$1000 \text{ c.c. of N alkali} \equiv \frac{0.2 \times 100}{1.51} \text{ g acid} = 132.45 \text{ g acid}$$

$\therefore$ Eq. weight of acid = 132.45

Since the acid is monobasic, therefore, mol. wt. = 132.45

The apparent molecular weight of the acid can be calculated from the given data, for which

$w_1 = 1$; $w_2 = 100$; $\Delta T = 0.1$; $K_f = 1.85$; $m_1 = ?$

Thus, $$m_1 = \frac{1000 K_f w_1}{w_2 \Delta T} = \frac{1000 \times 1.85 \times 1}{100 \times 0.168} = 110.1.$$

The dissociation of a monobasic acid (HA) is represented as :

$$\begin{array}{lllll} \text{HA} & \rightleftharpoons & \text{H}^+ & + & \text{A}^- \\ 1 & & 0 & & 0 \quad \text{(Before dissociation)} \\ 1-\alpha & & \alpha & & \alpha \quad \text{(After dissociation)} \end{array}$$

Now, $$\frac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

or $$\frac{110.1}{132.45} = \frac{1}{1+\alpha}$$

or $$\alpha = \frac{132.45}{110.1} - 1 = 1.203 - 1 = 0.203$$

∴ Degree of dissociation = **20.3%**

Ex. 24. ***1 g of a dibasic organic acid when dissolved in 100 ml of water caused a lowering of freezing point by 0.15°. 10 ml of the acid solution required 12 ml when titrated against N/10 alkali. Calculate the degree of ionisation of the acid, K_f for water = 1.89° per 1000 g of solvent.***

Sol. The normal molecular weight of the dibasic acid can be determined from the second part of the question. The normality (N_1) of the acid solution is calculated as follows :

$$\underset{\text{Acid}}{N_1V_1} = \underset{\text{Alkali}}{N_2V_2}$$

$$N_1 \times 10 = \frac{N}{10} \times 12$$

or $$N_1 = \frac{N \times 12}{10 \times 10} = \frac{3}{25}N$$

1 g of the acid is dissolved in 100 ml of water, therefore, strength of the solution is 10 g/litre.

∴ Strength (in g/litre) = Normalty (N_1) × Eq. wt. (E),

∴ $$10 = \frac{2}{25} \times E \quad \text{or} \quad E = \frac{250}{3}$$

Since the acid is dibasic, therefore,

$$\text{Mol. wt.} = \text{Eq. wt.} \times 2 = \frac{250}{3} \times 2 = 166.66.$$

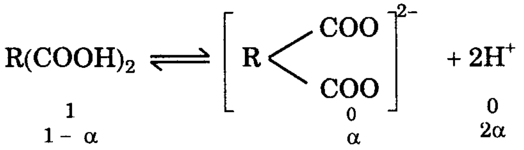
The apparent or observed molecular weight (m_1) of the acid can be calculated for which,

$$w_1 = 1; w_2 = 100; \Delta T = 0.15; m = ?$$

∴ $$m_1 = \frac{1000 K_f w_1}{w_1 . \Delta T} = \frac{1000 \times 1.89 \times 1}{100 \times 0.15}$$

$$= 126.0$$

The dissociation of a dibasic acid, $R(COOH)_2$ is represented as follows :



$$\begin{array}{cccccl} R(COOH)_2 & \rightleftharpoons & \left[R<\begin{matrix}COO\\COO\end{matrix}\right]^{2-} & + & 2H^+ & \\ 1 & & 0 & & 0 & \text{(Before dissociation)} \\ 1-\alpha & & \alpha & & 2\alpha & \text{(After dissociation)}\end{array}$$

Now, $\dfrac{\text{Observed mol. wt.}}{\text{Normal mol. wt.}} = \dfrac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$

$$\frac{126}{166.66} = \frac{1}{1+2\alpha}$$

or $\alpha = 0.1613$

∴ Degree of dissociation = **16.13%**

Ex. 25. ***1 g dibasic acid per 100 c.c. solution caused a lowering of freezing point by 0.15°. If 10 c.c. of this solution contains 1.2×10^{-3} equivalents of acid, calculate the degree of ionisation of acid ($K = 1.89°$ kg mole^{-1}).***

Sol.

∵ 10 ml of solution contains acid $= 1.2 \times 10^{-3}$ eq.

∴ 1000 ml of solution contains acid $= \dfrac{1.2 \times 10^{-3} \times 1000}{1000}$ eq

$$= 0.12 \text{ eq}$$

Amount of acid present in 1000 ml solution = 10 g

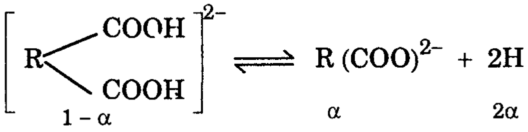
∴ Concentration = Equivalents × Equivalent weight

or $10 = 0.12 \times E$

or $E = \dfrac{10}{0.12} = \dfrac{1000}{12}$

∴ Normal molecular weight = Equivalent weight × Basicity

$$= \frac{1000}{12} \times 2 = \frac{1000}{6}$$



$$\begin{array}{ccccc} \left[R<\begin{matrix}COOH\\COOH\end{matrix}\right]^{2-} & \rightleftharpoons & R\,(COO)^{2-} & + & 2H \\ 1-\alpha & & \alpha & & 2\alpha \end{array}$$

Number of particles after dissociation

$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

Observed molecular weight

$$= \frac{1000K_f w_1}{w_2 \Delta T} = \frac{1000 \times 1.89 \times 1}{100 \times 0.15} = 126$$

$$\therefore \quad \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\frac{(1000/6)}{126} = \frac{1 + 2\alpha}{1}$$

or $$\alpha = 0.1613$$

$\therefore$ Degree of dissociation = **16.13%**

Ex. 26. ***The solution obtained by dissolving 1.25 g of sodium chloride in 50 g of water freezes at −1.53°C. Calculate the degree of dissociation of sodium chloride, given molar depression in 1000 g of water is 1.86° (Na = 23, Cl = 35.5).***

Sol. Normal molecular weight of NaCl = 23 + 35.5 = 58.5.

Observed molecular weight is determined as follows :

$$m_1 = \frac{1000K_f w_1}{w_2 . \Delta T}$$

Here, $K_f = 1.86$; $w_1 = 1.25$; $w_2 = 50$; $\Delta T = 0 - (1.53) = 1.53$

$$\therefore \quad m_1 = \frac{1000 \times 1.86 \times 1.25}{50 \times 1.53} = 30.39$$

NaCl dissociates as follows :

$$\begin{array}{lcccl} \text{NaCl} & \rightleftharpoons & \text{Na}^+ & + \ \text{Cl}^- & \\ 1 & & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & & \alpha & \alpha & \text{(After dissociation)} \end{array}$$

$$\therefore \quad \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\frac{58.5}{30.39} = \frac{1 - \alpha + \alpha + \alpha}{1} = \frac{1 + \alpha}{1}$$

or $$\alpha = 0.9249$$

$\therefore$ Degree of dissociation = **92.49%**

Ex. 27. ***The solution of 1 g of $AgNO_3$ in 50 g of water freezes at −0.348°C. Calculate the degree of ionisation of $AgNO_3$.*** **(Meerut 2006)**

Sol. Observed mol. wt. (m_1) of $AgNO_3$ is calculated as,

$$m_1 = \frac{1000K_f w_1}{w_2 \Delta T} = \frac{1000 \times 1.86 \times 1}{50 \times 0.348} = 106.89$$

Normal mol. wt. of $AgNO_3 = 108 + 14 + 48 = 170$

$$\begin{array}{cccl} AgNO_3 \rightleftharpoons & Ag^+ & + \; NO_3^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & \alpha & \alpha & \text{(After dissociation)} \end{array}$$

$$\frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

or $$\frac{170}{106.89} = \frac{1+\alpha}{1}$$

or $$\alpha = 0.5904$$

∴ Degree of ionisation = **59.04%**

Ex. 28. ***An aqueous solution develops an osmotic pressure of 1.28 atm. at 27°C. Calculate its freezing point. (Molal depression constant for water is 1.86°).***

Sol. From solution equation, we have, $P = \frac{w}{mV} \cdot RT$

or $$1.28 = \frac{w}{m \times 1} \times 0.0821 \times 300$$

or $$\frac{w}{m} = \frac{1.28}{0.0821 \times 300} = 0.0519$$

∴ The concentration of solute is 0.519 mole per litre.

Further, $$\Delta T = \frac{1000 K_f w_1}{w_2 m_1}$$

We have, $K_f = 1.86$, $w_1/m_1 = 0.0519$, $w_2 = 100\,g$.

∴ $$\Delta T = \frac{1000 \times 1.86 \times 0.0519}{1000} = 0.0965$$

∴ Freezing point of the solution

$$= \text{Freezing point of water} - \Delta T$$
$$= 0 - 0.0965 = -\mathbf{0.0965°C}$$

IMPORTANT FORMULAE

1. Osmotic pressure (P) of a solution is given by,

$$-P = \frac{w}{mV} \cdot RT$$

where, w = weight of solute in g, m = molecular weight of solute, V = volume of solution in litre ($1000\text{ cm}^3 = 1$ litre), T = absolute temperature (= temperature in centigrade + 273), R = gas constant, 0.0821 lit atm deg^{-1} mole^{-1}

2. If solutions 1 and 2 are isotonic, then,

$$\frac{w_1}{m_1V_1} = \frac{w_2}{m_2V_2}$$

3. From Raoult's law (for dilute solutions),

$$\frac{p - p_s}{p} = \frac{n_1}{n_2} = \frac{w_1m_2}{w_2m_1}$$

where, $p =$ vapour pressure of solvent, $p_s =$ vapour pressure of solution, $n_1 =$ no. of moles of solute, $n_2 =$ no. of moles of solvent, $w_1 =$ weight of solute of molecular weight m_1, $w_2 =$ weight of solvent of molecular weight m_2.

4. Relative lowering of vapour pressure

$$= \frac{\text{Lowering of V.P.}}{\text{V.P. of pure solvent}} = \frac{p - p_s}{p}$$

5. In Walter-Ostwald method, the molecular weight (m_1) of solute can be calculated from the following formula :

$$\frac{p - p_s}{p} = \frac{\text{Loss in weight of solvent bulb}}{\text{Loss in weight of (solvent + solution) bulbs}}$$

$$= \frac{\text{Loss in weight of solvent bulb}}{\text{Gain in weight of CaCl}_2\text{ tube}} = \frac{w_1m_2}{w_2m_1}$$

6. (a) Elevation of boiling point, ΔT

= (Boiling point of solution) – (Boiling point of solvent)

(b) (i) $$\Delta T = \frac{1000\,Kw_1}{w_2m_1}$$

where, $K =$ molecular elevation constant or elevation constant of 100 g of solvent, $w_1 =$ weight of solute, $w_2 =$ weight of solvent, $m_1 =$ molecular weight of solute,

(ii) $$\Delta T = \frac{1000\,K_b\,w_1}{w_2m_1}$$

where, $K_b =$ molal elevation constant or elevation constant for 1000 g of solvent.

(c) $$k = 100K = 1000K_b = \frac{RT^2}{L_e}$$

where, $k =$ elevation constant for 1 g of solvent, $T =$ boiling point of pure solvent, $L_e =$ latent heat of vaporisation per g of solvent.

7. (a) Depression in freezing point, ΔT

= (Freezing point of solvent) – (Freezing point of solution)

(b) (i) $$\Delta T = \frac{100\,Kw_1}{w_2m_1}$$

where, K = molecular depression constant or depression constant for 100 g of solvent.

(ii) $$\Delta T = \frac{1000 K_f w_1}{w_2 m_1}$$

where, K_f = molal depression constant or cryoscopic constant.

$$k = 100K$$

$$= 1000\, K_f = \frac{RT^2}{L_f}$$

where, k = depression constant for 1 g of solvent, T = freezing point of pure solvent, L_f = latent heat of fusion per g of solvent.

8. van't Hoff factor (i) is given by,

$$i = \frac{P_{obs}}{P_{nor}} = \frac{\Delta p_{obs}}{\Delta p_{nor}} = \frac{\Delta T_{obs}}{\Delta T_{nor}}$$

$$= \frac{\text{No. of particles after dissociation or association}}{\text{No. of particles before dissociation or association}}$$

$$= \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

EXERCISE

[I] Multiple Choice Questions

1. The following particles can only pass through a semi-permeable membrane :

(i) Solute particles (ii) Solvent particles

(iii) Complex ions (iv) Simple ions

2. The vapour pressure of a solution is :

(i) Proportional to its total pressure

(ii) Inversely proportional to concentration of solute

(iii) Proportional to temperature of solution

(iv) Proportional to absolute temperature of solution

3. The order of osmotic pressures of equal molecular concentrations of glucose, NaCl and $BaCl_2$ is : **(Meerut 2006)**

(i) Glucose > NaCl > $BaCl_2$ (ii) NaCl > $BaCl_2$ > Glucose

(iii) $BaCl_2$ > NaCl > Glucose (iv) Glucose > $BaCl_2$ > NaCl

4. In an aqueous solution 18 g glucose is present in 1000 g of solvent. It is :

(i) 1 molal (ii) 2 molal

(iii) 0.5 molal (iv) 0.1 molal

5. The cover of an egg is removed by means of dil. HCl and is then dipped in a saturated solution of salt. It will :
   (i) Shrink (ii) Expand
   (iii) Have no effect
   (iv) First shrink and then expands
6. 1.25 g of a non-electrolyte dissolved in 20 g water freezes at 271.94 K. If $K_f = 1.86°$, then the molecular weight of solute is :
   (i) 207.8 (ii) 209.6
   (iii) 179.8 (iv) 109.6
7. Assuming NaCl to be completely ionised the freezing point of 1 molal solution ($K_f = 1.86°$) is :
   (i) $-1.86°C$ (ii) $-3.72°C$
   (iii) $+1.86°C$ (iv) $+3.72°C$
8. The molal elevation constant of water is :
   (i) 5.15° (ii) 0.515°
   (iii) $(0.515 \times 2)°$ (iv) $(0.515 \times 3)°$
9. At 27°C the osmotic pressure of a solution containing 0.5 g/litre of a substance (mol. wt. = 150) is :
   (i) 0.082 atm (ii) 0.164 atm
   (iii) 0.328 atm (iv) 0.041 atm
10. The vant Hoff factors of glucose and NaCl are, respectively :
   (i) 1, 1 (ii) 2, 2
   (iii) 1, 2 (iv) 2, 1

ANSWERS

1. (ii), **2.** (ii), **3.** (ii), **4.** (iv), **5.** (i), **6.** (iv), **7.** (ii), **8.** (ii), **9.** (i), **10.** (iii).

[II] Short Answer Type Questions

1. Discuss van't Hoff theory of dilute solutions and derive general solution equation for dilute solution. **(Meerut 2007, 06)**
   [For answer, please see problem 8]
2. Mention the characteristics of ideal and non-ideal solutions.
   [For answer, please see problem 2]
3. Describe the differences between diffusion and osmosis.
   [For answer, please see problem 6]
4. How will you determine molecular weight of solute from osmotic pressure of the solution ?
   [For answer, please see problem 7]
5. State and explain Raoult's law of lowering of vapour pressure. How it is helpful in determining the molecular weight of a non-volatile solute ?
   [For answer, please see problem 10]

6. Write a short note on van't Haff factor.
   [For answer, please see problem 19]
7. Write a short note on abnormal molecular weight.
   [For answer, please see problem 19]
8. Write a short note on isotomic solutions.
   [For answer, please see problem 9]
9. How will you determine the molecular weight of a solute from isotomic solutions ?
   [For answer, please see problem 9]
10. What do you understand by abnormal osmotic pressure ?
    [For answer, please see problem 19]
11. How will derive a relation between elevation of boiling point and lowering of vapour-pressure thermodynamically ?
    [For answer, please see problem 14]
12. From thermodynamics point of view, derive a relation between depression of freezing point and molecular weight of solute.
    [For answer, please see problem 17]
13. Derive a relation between osmotic pressure and lowering of vapour pressure.
    [For answer, please see problem 12]
14. How is osmotic pressure measured in non-aqueous solvents ?
    [For answer, please see problem 7]
15. State and explain van't Hoff theory of dilute solutions.
    [For answer, please see problem 8]
16. A solution contains 25% ethanol, 50% acetic acid and 25% water by mass. Calculate the mole fraction of ethanol and acetic acid.
    [For answer, please refer to Ex. 5 after problem 1]
17. A solution of urea is isotonic with a 3% solution of glucose. Find the concentration of the urea solution.
    [For answer, please refer to Ex. 5, after problem 9]
18. 18.2 gm of an organic compound was dissolved in 100 gm of water at 50°C. The lowering of vapour pressure produced was 5 mm Hg. Calculate the molecular weight of organic compound. The vapour pressure of water at 50°C is 92 mm Hg.
    [For answer, please refer to Ex. 7, after problem 12]

[III] Very Short Answer Type Questions

1. Define normality.
   [For answer, please see problem 1]
2. Define molarity. [For answer, please see problem 1]
3. Define molality. [For answer, please see problem 1]
4. What do you understand by mole fraction of a solution ?
   [For answer, please see problem 1]

5. Define molal elevation constant. **(Meerut 2005)**
[For answer, please see problem 15]
6. Define molar depression constant.
[For answer, please see problem 18]
7. Define abnormal molecular weight. **(Meerut 2007)**
[For answer, please see problem 19]
8. Define activity and activity coefficient.
[For answer, please see problem 5]
9. Define osmosis. [For answer, please see problem 6]
10. Define osmotic pressure of a solution.
[For answer, please see problem 7]
11. What is the effect of concentration on osmotic pressure ?
[For answer, please see problem 7]
12. How osmotic pressure of a solution is affected by temperature ?
[For answer, please see problem 7]
13. State van't Hoff theory of dilute solutions.
[For answer, please see problem 8]
14. What are isotomic solutions ? [For answer, please see problem 9]
15. Define Raoult's law of lowering of vapour pressure.
[For answer, please see problem 10]
16. Give the relation between molal elevation constant and latent heat of vaporisation. [For answer, please see problem 15]
17. Give the relation between molal depression constant and latent heat of fusion. [For answer, please see problem 18]
18. Define relative lowering of vapour pressure.
[For answer, please see problem 10]
19. Calculate the molal depression constant for water.
[For answer, please refer to Ex. 1 after problem 18]
20. Calculate the molal elevation constant for water.
[For answer, please refer to Ex. 1, after problem 15]

❑❑❑

COMMON LOGARITHMS $\log_{10} x$

x	0	1	2	3	4	5	6	7	8	9	Δ_m	1	2	3	4	5	6	7	8	9
											+	ADD								
10	.0000	0043	0086	0128	0170	0212					42	4	8	13	17	21	25	29	34	38
						0212	0253	0294	0334	0374	40	4	8	12	16	20	24	28	32	36
11	.0414	0453	0492	0531	0569	0607					39	4	8	12	16	19	23	27	31	35
						0607	0645	0682	0719	0755	37	4	7	11	15	19	22	26	30	33
12	.0792	0828	0864	0899	0934	0969					35	4	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	34	3	7	10	14	17	20	24	27	31
13	.1139	1173	1206	1239	1271	1303					33	3	7	10	13	16	20	23	26	30
						1303	1335	1367	1399	1430	32	3	6	10	13	16	19	22	26	29
14	.1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	30	3	6	9	12	15	18	21	24	27
15	.1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	28	3	6	8	11	14	17	20	22	25
16	.2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	26	3	5	8	10	13	16	18	21	23
17	.2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	25	2	5	7	10	12	15	17	20	22
18	.2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	24	2	5	7	10	12	14	17	19	22
19	.2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	22	2	4	7	9	11	13	15	18	20
20	.3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	21	2	4	6	8	11	13	15	17	19
21	.3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	20	2	4	6	8	10	12	14	16	18
22	.3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	19	2	4	6	8	10	11	13	15	17
23	.3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	18	2	4	5	7	9	11	13	14	16
24	.3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	18	2	4	5	7	9	11	13	14	16
25	.3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	17	2	3	5	7	9	10	12	14	15
26	.4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	16	2	3	5	6	8	10	11	13	14
27	.4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	16	2	3	5	6	8	10	11	13	14
28	.4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	15	2	3	5	6	8	9	11	12	14
29	.4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	15	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	14	1	3	4	6	7	8	10	11	13
31	.4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	14	1	3	4	6	7	8	10	11	13
32	.5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	13	1	3	4	5	7	8	9	10	12
33	.5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	13	1	3	4	5	6	8	9	10	12
34	.5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	13	1	3	4	5	6	8	9	10	12
35	.5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	12	1	2	4	5	6	7	8	10	11
36	.5563	5573	5587	5599	5611	5623	5635	5647	5668	5670	12	1	2	4	5	6	7	8	10	11
37	.5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	12	1	2	4	5	6	7	8	10	11
38	.5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	11	1	2	3	4	6	7	8	9	10
39	.5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	11	1	2	3	4	6	7	8	9	10
40	.6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	11	1	2	3	4	8	7	8	9	10
41	.6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	10	1	2	3	4	8	6	7	8	9
42	.6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	10	1	2	3	4	8	6	7	8	9
43	.6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	10	1	2	3	4	8	6	7	8	9
44	.6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	10	1	2	3	4	8	6	7	8	9
45	.6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	10	1	2	3	4	8	6	7	8	9
46	.6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	9	1	2	3	4	8	5	6	7	8
47	.6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	9	1	2	3	4	8	5	6	7	8
48	.6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	9	1	2	3	4	4	5	6	7	8
49	.6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	9	1	2	3	4	4	5	6	7	8

No.	log		No.	log
n = 3.14159	0.49715	In x = $\log_e x$ = (1/M) $\log_{10} x$	(1/M) = 2.30259	0.36222
e = 2.71828	0.43429	$\log_x$ = $\log_{10} x$ = M $\log_e x$	M = 0.43429	1.63778

p	1	2	3	4	5	6	7	8	9	10
$\log e^p$	0.4343	0.8686	1.3029	1.7372	2.1715	2.6058	3.0401	3.4754	3.9087	4.3429
$\log e^{-p}$	1.5657	1.1314	2.6971	2.2628	3.8285	3.3942	4.9599	4.5256	4.0913	5.6571

COMMON LOGARITHMS $\log_{10} x$

x	0	1	2	3	4	5	6	7	8	9	Δ_m	1	2	3	4	5	6	7	8	9
											+	ADD								
50	.6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	9	1	2	3	4	4	5	6	7	8
51	.7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	8	1	2	2	3	4	5	6	6	7
52	.7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	8	1	2	2	3	4	5	6	6	7
53	.7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	8	1	2	2	3	4	5	6	6	7
54	.7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	8	1	2	2	3	4	5	6	6	7
55	.7404	7412	7419	7427	7433	7443	7451	7459	7466	7474	8	1	2	2	3	4	5	6	6	7
56	.7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	8	1	2	2	3	4	5	6	6	7
57	.7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	8	1	2	2	3	4	5	6	6	7
58	.7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	8	1	2	2	3	4	5	6	6	7
59	.7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	7	1	1	2	3	4	4	5	6	6
60	.7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	7	1	1	2	3	4	4	5	6	6
61	.7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	7	1	1	2	3	4	4	5	6	6
62	.7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	7	1	1	2	3	3	4	5	6	6
63	.7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	7	1	1	2	3	3	4	5	6	6
64	.8062	8069	8075	8082	8089	8096	8101	8109	8116	8182	7	1	1	2	3	3	4	5	6	6
65	.8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	7	1	1	2	3	3	4	5	6	6
66	.8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	7	1	1	2	3	3	4	5	6	6
67	.8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	6	1	1	2	2	3	4	4	5	5
68	.8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	6	1	1	2	2	3	4	4	5	5
69	.8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	6	1	1	2	2	3	4	4	5	5
70	.8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	6	1	1	2	2	3	4	4	5	5
71	.8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	6	1	1	2	2	3	4	4	5	5
72	.8573	8579	8585	8691	8597	8603	8609	8615	8621	8627	6	1	1	2	2	3	4	4	5	5
73	.8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	6	1	1	2	2	3	4	4	5	5
74	.8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	6	1	1	2	2	3	4	4	5	5
75	.8751	8756	8762	9768	8774	8779	8785	8791	8797	8802	6	1	1	2	2	3	4	4	5	5
76	.8808	8814	8820	8825	8831	8837	8842	8843	8854	8859	6	1	1	2	2	3	4	4	5	5
77	.8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	6	1	1	2	2	3	4	4	5	5
78	.8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	6	1	1	2	2	3	4	4	5	5
79	.8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	6	1	1	2	2	3	4	4	5	5
80	.9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	5	1	1	2	2	3	3	4	4	5
81	.9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	5	1	1	2	2	3	3	4	4	5
82	.9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	5	1	1	2	2	3	3	4	4	5
83	.9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	5	1	1	2	2	3	3	4	4	5
84	.9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	5	1	1	2	2	3	3	4	4	5
85	.9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	5	1	1	2	2	3	3	4	4	5
86	.9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	5	1	1	2	2	3	3	4	4	5
87	.9395	9400	9305	9410	9415	9420	9425	9430	9435	9440	5	0	1	1	2	2	3	3	4	4
88	.9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	5	0	1	1	2	2	3	3	4	4
89	.9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	5	0	1	1	2	2	3	3	4	4
90	.9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	5	0	1	1	2	2	3	3	4	4
91	.9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	5	0	1	1	2	2	3	3	4	4
92	.9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	5	0	1	1	2	2	3	3	4	4
93	.9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	5	0	1	1	2	2	3	3	4	4
94	.9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	5	0	1	1	2	2	3	3	4	4
95	.9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	5	0	1	1	2	2	3	3	4	4
96	.9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	4	0	1	1	2	2	2	3	3	4
97	.9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	4	0	1	1	2	2	2	3	3	4
98	.9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	4	0	1	1	2	2	2	3	3	4
99	.9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	4	0	1	1	2	2	2	3	3	4

ANTILOGARITHMS 10^x

x	0	1	2	3	4	5	6	7	8	9	Δm	1	2	3	4	5	6	7	8	9
											+	ADD								
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	2	0	0	1	1	1	1	1	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	2	0	0	1	1	1	1	1	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	2	0	0	1	1	1	1	1	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	2	0	0	1	1	1	1	1	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	3	0	1	1	1	1	2	2	2	3
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	3	0	1	1	1	1	2	2	2	3
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	3	0	1	1	1	1	2	2	2	3
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	3	0	1	1	1	1	2	2	2	3
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	3	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	3	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	3	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	3	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	3	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	3	0	1	1	1	2	2	2	2	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	3	0	1	1	1	2	2	2	2	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	3	0	1	1	1	2	2	2	2	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	3	0	1	1	1	2	2	2	2	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	4	0	1	1	2	2	2	3	3	4
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	4	0	1	1	2	2	2	3	3	4
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	4	0	1	1	2	2	2	3	3	4
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	4	0	1	1	2	2	2	3	3	4
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	4	0	1	1	2	2	2	3	3	4
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	4	0	1	1	2	2	2	3	3	4
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	4	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	4	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	4	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	4	0	1	1	2	2	2	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	4	0	1	1	2	2	2	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	4	0	1	1	2	2	2	3	3	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	4	0	1	1	2	2	2	3	3	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	5	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	5	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	5	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	5	1	1	2	2	3	3	4	4	5
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	5	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	5	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	5	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	6	1	1	2	2	3	4	4	5	5
.38	2399	2404	2410	2415	2421	2427	2432	2338	2443	2449	6	1	1	2	2	3	4	4	5	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	6	1	1	2	2	3	4	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	6	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	6	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	6	1	1	2	2	3	4	4	5	5
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	6	1	1	2	2	3	4	4	5	5
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	6	1	1	2	2	3	4	4	5	5
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	7	1	1	2	3	3	4	5	6	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	7	1	1	2	3	3	4	5	6	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	7	1	1	2	3	3	4	5	6	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	7	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	7	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS 10^x

x	0	1	2	3	4	5	6	7	8	9	Δ_m	1	2	3	4	5	6	7	8	9
											+	ADD								
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	7	1	1	2	3	4	4	5	6	6
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	8	1	2	2	3	4	5	6	6	7
.52	3311	3319	3327	3334	3342	3550	3357	3365	3373	3381	8	1	2	2	3	4	5	6	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	8	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	8	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	8	1	2	2	3	4	5	6	6	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	8	1	2	2	3	4	5	6	6	7
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	9	1	2	3	4	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	9	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3926	3945	3954	3863	3972	9	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	9	1	2	3	4	5	5	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	10	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	10	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	10	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	10	1	2	3	4	5	6	7	8	9
65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	10	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	11	1	2	3	4	5	7	8	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	11	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4883	11	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	11	1	2	3	4	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	12	1	2	4	5	6	7	8	10	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	12	1	2	4	5	6	7	8	10	11
.72	5248	560	5272	5284	5297	5309	5321	5335	5346	5358	12	1	2	4	5	6	7	8	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	12	1	2	4	5	6	7	8	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	13	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	13	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	13	1	3	4	5	7	8	9	10	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	14	1	3	4	6	7	8	10	11	13
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	14	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	14	1	3	4	6	7	8	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	15	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	15	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	15	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	16	2	3	5	6	8	10	11	13	14
.84	6918	6934	6950	6996	6982	6998	7015	7731	7047	7063	16	2	3	5	6	8	10	11	13	14
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	16	2	3	5	6	8	10	11	13	14
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	17	2	3	5	7	8	10	12	14	15
.87	7413	7430	7447	7564	7482	7499	7516	7534	7551	7568	17	2	3	5	7	9	10	12	14	15
88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	18	2	4	5	7	9	11	13	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	18	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	18	2	4	5	7	9	11	13	14	16
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	19	2	4	6	8	10	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	19	2	4	6	8	10	11	13	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	20	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	20	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	21	2	4	6	8	10	13	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	21	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	22	2	4	7	9	11	13	15	18	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	22	2	4	7	9	11	13	15	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	23	2	5	7	9	11	14	16	18	21